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# COMPOSITION OF SHALE-OIL NAPHTHA

By G. U. Dinneen, R. A. Van Meter, J. R. Smith, C. W. Bailey,
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By

G. U. Dinneen,[2] R. A. Van Meter,[3] J. R. Smith,[4] C. W. Bailey,[4] G. L. Cook,[2] C. S. Allbright,[5] and John S. Ball [6]

## *Summary*

THIS REPORT describes the analysis of shale-oil naphthas and discusses their composition, based on investigation by the Federal Bureau of Mines. Individual compounds identified in this investigation are listed, together with those reported previously in the literature. Also, quantitative data are given on the occurrence of individual compounds and groups of related compounds. A comprehensive analysis is presented for a naphtha from shale oil produced in an N–T–U (Nevada-Texas-Utah) retort from Green River shale. Results of less detailed analyses are given for 13 other naphthas from Colorado shale oils, for 1 naphtha from Tennessee shale oil, and for 26 naphthas from oils from foreign countries. A description of the general analytical approach used and of techniques developed especially for analyzing shale-oil distillates is included.

Naphthas from Colorado shale oils generally contain 85 to 95 pct. hydrocarbon compounds and 5 to 15 pct. sulfur-, nitrogen-, and oxygen-containing compounds. In the present work, 12 saturated hydrocarbons, 7 olefinic hydrocarbons, 19 aromatic hydrocarbons, 18 thiophenes, 1 sulfide, 16 pyridines, quinoline, 4 pyrroles, 3 nitriles, 13 phenols, 2 carboxylic acids, and benzofuran were identified. The saturates and olefins were mostly straight-chain compounds. For the aromatic hydrocarbons and the heterocyclic series where a number of compounds were identified, most of the lower boiling isomers were included. Compounds having substitution in the 1,4- and 1,2,4-positions were more prevalent, comprising, for example, three-fourths of the polyalkylbenzenes that were identified.

Data on the quantitative distribution of compounds are often more important in characterizing a material than are qualitative identifications, because qualitative findings may include compounds present only in very small quantities. Analysis of a naphtha from N–T–U shale oil, which was the most comprehensive obtained in this study, showed that the saturated hydrocarbons consisted of 3 parts straight-chain compounds to 2 parts branched-chain compounds to 1 part cyclic compounds; the olefinic hydrocarbons had these classes of compounds present in about equal quantities, and the quantity of monosubstituted aromatic compounds decreased with increase in molecular weight. The molecular-weight distribution of the hydrocarbons showed a concentration in the range of compounds containing 10 or 11 carbon atoms per molecule. Quantitative estimates for thiophenes indicated a preferred substitution pattern: 2-Monosubstitution predominated over 3-monosubstitution; 2,5-disubsti-

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tution predominated over other types of disubstitution; and 2,3,5-trisubstitution predominated over 2,3,4-trisubstitution.

The composition of the N–T–U naphtha was compared with that from a Scottish shale oil and with that from two other Colorado shale oils, Pumpherston and 1,200° F. high-temperature retorting. Although the analyses were not all made in exactly the same way, it appeared that the compositions of the naphthas, except for those from high-temperature retorting, were similar. The naphtha from high-temperature retorting was more aromatic than the others.

Less comprehensive analyses were obtained on several other naphthas from Colorado shale oils. On the basis of hydrocarbon composition, the naphthas could be grouped into those from oils produced at ordinary retorting temperatures and those from oils produced at higher retorting temperatures. The naphthas from low-temperature oils were similar to the N–T–U naphtha discussed previously. Naphthas from high-temperature oils were more aromatic. The aromaticity increased as the retorting temperature was raised, so that naphtha from oil produced at 1,500° F. was almost entirely aromatic. The distribution of aromatic hydrocarbons by molecular-weight groups showed a shift to lower boiling compounds as the retorting temperature was increased. This same shift was shown in the phenols. On the basis of sulfur and nitrogen contents, the naphthas did not fall into groups as they did on the basis of hydrocarbon composition. Although there was a fairly large variation in the values for sulfur and nitrogen in the naphthas, it appeared that the quantities of these elements were essentially independent of the retorting method.

Several naphthas obtained by thermal cracking of Colorado shale oils were analyzed. The cracked naphthas showed variations in hydrocarbon group compositions depending on severity of cracking conditions and whether or not recycle operations were used. However, within the hydrocarbon groups the proportions of types of compounds were similar to those reported for the N–T–U naphtha.

Naphthas and gasolines from several foreign countries were analyzed. The results indicated that, as with the Colorado naphthas, the sulfur and nitrogen contents depended primarily on shale characteristics rather than retorting method. Comparison of results of analyses on naphthas from oils produced in similar retorts from different shales showed that the shale characteristics also had some effect on hydrocarbon composition. Some of the samples from foreign countries were finished gasolines. These had a high olefin content, practically no nitrogen, and a sulfur content that was lower than the corresponding raw naphtha but higher than an average petroleum gasoline produced in the United States.

The general analytical scheme and special methods developed during this work are described. The naphtha was treated consecutively with aqueous base and acid to extract tar acids and tar bases, which were recovered from the extracts. The tar acids, tar bases, and neutral oil from the extractions were each distilled into narrow-boiling fractions. The composition of these fractions was determined by a combination of physical, chemical, and spectral techniques. Special methods developed were: An adsorption technique for determining hydrocarbon groups; a modified Kjeldahl procedure for determining total nitrogen; a nonaqueous titration procedure for determining basic nitrogen; and a systematic procedure for identifying alkylthiophenes.

# INTRODUCTION

Oil shales are mixtures of organic and inorganic material. The organic material is composed of carbon, hydrogen, oxygen, sulfur, and nitrogen. It has limited solubility in ordinary solvents, and upon heating is decomposed into gas, shale oil, and residual carboniferous material that remains on the spent shale. The resulting oil resembles petroleum in that it is composed of hydrocarbons and sulfur, nitrogen, and oxygen derivatives of hydrocarbons. However, the nonhydrocarbon content is generally greater than in petroleum, and the hydrocarbons are less saturated than those of petroleum.

In some other countries, oil shale was a source of liquid fuel even before the first successful oil well was drilled in the United States in 1859. The first patent concerning retorting was issued in 1794, and a commercial operation was started in France in 1835. Although some commercial ventures, notably in Scotland, have operated continuously for years, many made only short-lived efforts to compete with petroleum. There was little activity in the field during the years when petroleum was relatively easy to find and the demand for it was limited. At present, commercial oil-shale operations are being conducted in Scotland, Sweden, South Africa, Spain, and Russia. However, the generally small size and limited financial backing of many shale operations have not permitted adequate research into the composition of shale oil. Hence, the fundamental data to form a sound technological basis for an industry have not been available.

In the United States, oil shale and coal provide vast reserves of materials that are potentially capable of supplying liquid fuels to supplement those obtained from petroleum. A major objective of the Synthetic Liquid Fuels and normal minerals programs of the Bureau of Mines is to provide technical data on which to base eventual exploitation of these materials. The particular phase of this objective covered by this paper is to provide data on the composition of the naphtha fraction from shale oil.

Naphtha is a generic term that is defined in petroleum technology as a fraction not less than 10 pct. of which distills below 175° C. and not less than 95 pct. of which distills below 240° C.[7] The compounds in such a fraction will usually contain from 5 to 13 carbon atoms, so it is the occurrence of these compounds in shale oil that is discussed in this paper, regardless of whether a naphtha fraction, as such, was distilled from an oil. Since 200° C. is frequently used as the cut temperature when distilling a naphtha from an oil, the quantities of compounds having boiling points above this temperature that are present in such a naphtha are not the total quantities that were present in the original shale oil.

Shale oil is produced by the destructive distillation of the organic material in oil shale so that all shale-oil distillates contain the types of compounds normally considered to result from thermal cracking reactions. However, in this report naphthas are considered in two classes—primary and cracked. A primary naphtha is obtained from crude shale oil by distillation at temperatures minimizing thermal reactions. A cracked naphtha is obtained from a charge stock that has been subjected to the temperatures and pressures customarily associated with thermal cracking processes.

Shale oils and the naphthas distilled from them are usually indentified by the name of the retorting process used to produce the oil. Since there are many retorting processes, it is convenient to group them when attempting to correlate the effects of retorting variables with chemical composition of the oils produced. A classification based on method of heat transfer has been suggested.[8] The classes are: I. Those in which heat is transferred to the shale through a wall; II. those in which heat is transferred to the shale from combustion gases generated in the retort; III. those in which heat is transferred to the shale by passing previously heated gases or liquids through the shale bed; and IV. those in which heat is transferred by introduction of hot solids into the retorting bed.

Because shale oil and crude petroleum differ in composition, fuels produced from them also will differ. The literature on petroleum composition is extensive, but references to the composition of shale-oil distillates are few and usually limited in scope to compounds, such as pyridines, that are rather easily isolated and identified because of their reactivity. This paper presents available information on the composition of shale-oil naphtha.

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## ORGANIZATION OF REPORT

This report is divided into four main sections. Some of the data resulting from investigations in this laboratory are presented in each of the first two sections, but in different context to illustrate the appropriate discussion.

The first section discusses the present knowledge of the composition of shale-oil naphtha based both on results from Bureau of Mines laboratories and on information from literature. The discussion is divided into two portions—qualitative identifications and quantitative determinations. The qualitative portion lists the compounds that have been identified in shale-oil naphtha and the geographical source of the oil from which the naphtha was distilled. The compounds are presented in four tables—hydrocarbons, sulfur-containing compounds, nitrogen-containing compounds, and oxygen-containing compounds—with the pertinent references as footnotes to the tables. The quantitative portion discusses the distribution of individual compounds or groups of related compounds in several primary naphthas and in one thermally cracked naphtha. In addition, results are reported for hydrocarbon-group determinations on naphthas from crude-shale-oil analyses on a number of Colorado and foreign oils.

The second section describes the analytical investigations that were performed in this laboratory on 41 naphthas. In this section, the naphthas are generally identified by the name of the retorting process that was used to produce the oil from which they were distilled. The extent of the work done on the naphthas varied because in some instances an investigation was specifically aimed toward determining the composition of the naphtha, whereas in other instances an investigation yielded data on the naphtha fraction as an incidental part of a larger investigation. The naphthas are discussed in order of the amount of work done on them, with the one examined most extensively given first.

The third section describes the general analytical procedure used on the naphthas. The procedure is essentially a schematic arrangement of established techniques designed to resolve the naphthas into fractions sufficiently homogeneous for characterization.

The fourth section gives methods that were developed specifically for the analysis of shale-oil naphthas. These methods are: A silica-gel-adsorption technique for determining hydrocarbon groups; a modified Kjeldahl procedure for determining total nitrogen; a nonaqueous titration procedure for determining basic nitrogen; and a systematic procedure for identifying alkylthiophenes.

# COMPONENTS OF SHALE-OIL NAPHTHAS

Naphtha from Colorado shale oil generally consists of 85 to 95 pct. hydrocarbon compounds and 5 to 15 pct. of compounds containing sulfur, nitrogen, or oxygen. The same types of compounds are present in petroleum and coal-tar distillates, but the relative quantities are different in the three materials. Because many factors affect the composition, it is impossible to select samples whose compositions are typical of these materials. However, the data in figure 1 indicate, in a general way, the composition relationships among them.

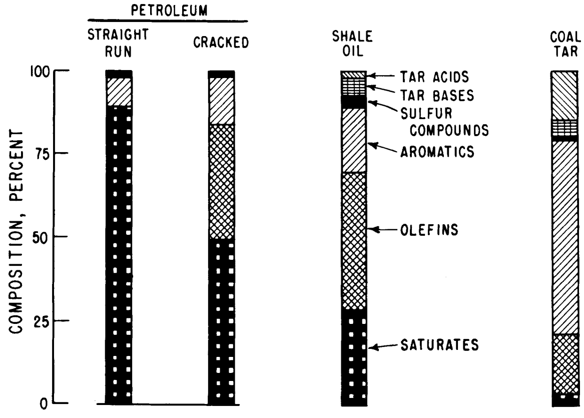

FIGURE 1.—Approximate Composition of Naphthas From Petroleum, Shale Oil, and Coal Tar.

The contents of saturates and aromatics in the shale-oil naphtha are intermediate between those in the other two types of material. The shale-oil naphtha has an olefin content resembling that of cracked petroleum naphtha, but its total tar-acid and tar-base content is more like that of coal tar.

## COMPOUND IDENTIFICATION

The individual hydrocarbons in shale-oil naphtha that have been identified by previous workers and those identified in this investigation are listed in table 1. In addition to these individual compounds, many workers[9–27] have mentioned the presence of groups of isomeric compounds for which only empirical formulas were determined.

For the Colorado naphthas a larger number of individual compounds was identified in the aromatic group than in any of the other hydrocarbon groups. Hence, some trends in the occurrence of aromatic isomers in these naphthas were observed. The quantities of aromatic compounds having a single alkyl substituent decreased with increase in molecular weight so that in the $C_{10}$-benzene range the butylbenzenes were not present in sufficient quantities to be detected. Of the polyalkyl substituted benzenes only disubstituted and trisubstituted compounds were identified, as the lowest boiling tetrasubstituted compound boiled above the range where identifications could be made with the techniques available at the time the work was done. The 1,4- and 1,2,4-positions were favored, as compounds having substituents in these positions comprised about three-fourths of the polyalkylbenzenes that were identified.

The sulfur in the Colorado shale-oil naphthas was predominantly in the form of thiophenes, with a much smaller quantity in the form of

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TABLE 1.—*Hydrocarbons identified in shale-oil naphtha*

(X = Identified in this investigation)

| Compound | Previous identification[1] | This investigation |
|---|---|---|
| Saturates: | | |
| n-Pentane | Sc,[2–4] Ma[5] | X |
| iso-Pentane | Sc,[2–4] Ma[5] | X |
| Methylcyclobutane | Sc[4] | |
| Cyclopentane | Sc[2, 4] | |
| n-Hexane | Sc,[2, 3, 6] Es[7] | X |
| 2-Methylpentane | Sc[2] | |
| 3-Methylpentane | Sc[2] | |
| 2,3-Dimethylbutane | Ma[8] | |
| Methylcyclopentane | Sc,[2, 6] Es[7] | |
| Cyclohexane | Sc,[2, 6] Es[7, 9] | |
| n-Heptane | Sc,[2, 3, 6] Es,[7] Ru[10] | X |
| 3-Methylhexane | Sc[2] | |
| 3-Ethylpentane | Ma[11] | |
| 1,2-Dimethylcyclopentane | Es[7] | |
| 1,3-Dimethylcyclopentane | Es[7] | |
| Ethylcyclopentane | Sc[2] | X |
| Methylcyclohexane | Sc,[2, 4] Es,[7] Ma[10] | X |
| n-Octane | Sc,[2] Es,[7] Ma[12] | X |
| 2-Methylheptane | Sc,[2] Es[7] | |
| 3-Methylheptane | Sc,[2] Es[7] | |
| 4-Methylheptane | Sc,[2] Es[7] | |
| n-Propylcyclopentane | Sc,[2] Es[7] | |
| Ethylcyclohexane | Sc,[2] Es[7] | |
| 1,2-Dimethylcyclohexane | Es[7] | |
| 1,3-Dimethylcyclohexane | Es[7] | |
| n-Nonane | Es,[7] Ma[13] | X |
| 2-Methyloctane | Es[7] | |
| 3-Methyloctane | Es[7] | |
| 4-Methyloctane | Es[7] | |
| 3,3-Dimethylheptane | Ma[13] | |
| 3-Ethylheptane | Es[7] | |
| 3,3-Diethylpentane | Ma[12] | |
| n-Decane | Es,[7] Ma[14] | X |
| 3-Ethyloctane | Es[7] | |
| n-Undecane | Es,[7] Ma[15] | X |
| n-Dodecane | Ma,[16] Es[17, 18] | X |
| n-Tridecane | Ma,[16] Es[17, 18] | X |
| Olefins: | | |
| Pentene-1 | Sc,[2] Ma,[5] Sw[19] | X |
| Pentene-2 | Sc,[2] Ma,[5] Sw[19] | |
| 2-Methylbutene-1 | Ma[5] | |
| 2-Methylbutene-2 | Sc,[2] Sw[19] | |
| Cyclopentene | Sc[2] | |
| Pentadiene-1,3 | Sc,[2] Sp[20] | |
| 2-Methylbutadiene-1,3 | Sc,[2] Sp[20] | |
| Cyclopentadiene | Sp,[20] Au,[21] Fr[22] | |
| Hexene-1 | Sc[2] | X |
| Hexene-2 | Sc,[2] Es,[7] Ma[23] | |
| Hexene-3 | Sc,[2] Es[7] | |
| 2-Methylpentene | Ma[23] | |
| 2,3-Dimethylbutene-2 | Ma[23] | |
| Methylcyclopentene | Sc[2] | |
| Cyclohexene | Sc,[2] Es[8] | |
| Hexadiene-1,3 | Sc[2] | |
| Hexadiene-2,4 | Sc[2] | |
| 1,1-Dimethylbutadiene | Sp[20] | |
| 1,2-Dimethylbutadiene | Sp[20] | |
| 1,3-Dimethylbutadiene | Sp[20] | |
| 2,3-Dimethylbutadiene | Sp[20] | |
| Cyclohexadiene-1,3 | Sp[20] | |
| Heptene-1 | Sc,[2] Ma,[24] Ru[25] | X |
| Heptene-2 | Sc,[2] Es,[7] Ma[24] | |
| Heptene-3 | Sc[2] | |
| 3-Ethylpentene-2 | Ma[24] | |
| Octene-1 | Sc,[2] Es,[7] Ru[25] | X |
| Octene-2 | Sc,[2] Ma[26] | |
| Octene-3 | Sc[2] | |
| Octene-4 | Sc,[2] Es[7] | |
| Octadiene-2,6 | Ma[26] | |
| 2-Methylheptadiene-3,5 | Ma[26] | |
| Nonene-1 | Ru[25] | X |
| Nonene-2 | Ma[13] | |
| 2,5,5-Trimethylhexene-2 | Es[7] | |
| Decene-1 | | X |
| Decene-2 | Ma[14] | |
| Dicyclopentadiene | Au[21] | |
| Undecene-1 | Ma[15] | X |
| Undecene-2 | Ma[15] | |
| Dodecene | Ru[27] | |
| Tridecene | Ru[27] | |
| Aromatics: | | |
| Benzene | Sc,[2–4, 6] Es,[7] Ma,[9] Au,[21] Sw,[28] Ru,[29–34] Pa.[35] | X |
| Toluene | Sc,[2–4, 6] Es,[7] Ma,[11] Ru,[29–33] Pa,[35] Sw.[33] | X |
| Ethylbenzene | Sc,[2] Ru[29] | X |
| o-Xylene | Sc,[2] Es,[7] Ru[29] | X |
| m-Xylene | Sc,[2, 3] Es,[7] Ma,[12, 13] Ru[29] | X |
| p-Xylene | Sc,[2] Es,[7] Ru,[29] Sw[36] | X |
| Styrene | | X |
| n-Propylbenzene | Es[7] | X |
| Isopropylbenzene | Sc[3] | X |
| 1-Methyl-2-ethylbenzene | Es[7] | |
| 1-Methyl-3-ethylbenzene | Es[7] | X |
| 1-Methyl-4-Ethylbenzene | | X |
| 1,2,3-Trimethylbenzene | Es[7] | |
| 1,2,4-Trimethylbenzene | Es,[7] Sw[36] | X |
| 1,3,5-Trimethylbenzene | Ma[14] | X |
| 1,3-Diethylbenzene | | X |
| 1,4-Diethylbenzene | | X |
| Indene | Au[21] | X |
| Naphthalene | Au,[21] Ru,[29, 33] Pa,[35] Es[18, 37–39] | X |
| 1-Methylnaphthalene | Es,[18, 37–39] Ge[40] | X |
| 2-Methylnaphthalene | Es,[18, 37–39] Ge[40] | X |

See footnotes at end of table.

TABLE 1.—*Hydrocarbons identified in shale-oil naphtha*—Continued

(X = Identified in this investigation)

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[1] Abbreviations refer to location of origin of shale: Au, Australia; Es, Estonia; Ge, Germany; Ma, Manchuria; Pa, Palestine; Ru, U.S.S.R.; Sc, Scotland; Sp, Spain; Sw, Sweden.

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the next most abundant group, the cyclic sulfides. Eighteen thiophenes and a cyclic sulfide were identified in this study. These compounds, together with sulfur compounds previously reported in the literature, are listed in table 2.

Eight thiophenes identified in the present work have not been reported by other workers. Most of these compounds are of higher molecular weight than those previously reported, and their identification was facilitated by the new techniques developed for this study. All but four of the thiophenes reported by other workers have been identified in the present investigation. These four are 2-n-propylthiophene, 3-n-propylthiophene, 3-isopropylthiophene, and 2-n-butylthiophene. Some evidence was found in the present work for all of these except 3-isopropylthiophene, but positive identifications were not obtained.

Hydrogenation of 16 of the 18 thiophenes reported in this paper would result in normal alkanes or mono-methyl alkanes. These two types of compounds are abundant in shale oil, suggesting that a possible explanation for the formation of thiophenes in shale oil would be by a reversal of the mechanism, that is, by dehydrogenation of alkanes followed by cyclization in the presence of sulfur. Among other possibilities are degradation of larger sulfur-containing molecules present in kerogen and equilibration of retorting products according to thermodynamic requirements. Data were not available to permit making a choice among possibilities.

Results of the present study showed the presence of three classes of nitrogen compounds: Pyridines, pyrroles, and nitriles. Individual members identified in these classes are compared in table 3 with those reported by

TABLE 2.—*Sulfur-containing compounds identified in shale-oil naphtha*

(X = Identified in this investigation)

| Compound | Previous identification [1] | This investigation |
|---|---|---|
| Thiophene | En,[2] Ru,[3] [4] Sw [5] | X |
| 2-Methylthiophene | En,[2] Ru,[3] [4] Ge,[6] Un [7] | X |
| 3-Methylthiophene | Sw,[5] Ge [6] | X |
| 2, 3-Dimethylthiophene | En,[2] Ru,[3] [4] Ge [6] | X |
| 2, 4-Dimethylthiophene | | X |
| 2, 5-Dimethylthiophene | Un [7] | X |
| 3, 4-Dimethylthiophene | Ge [6] | X |
| 2-Ethylthiophene | En,[2] Ru,[4] Ge,[6] Un [7] | X |
| 3-Ethylthiophene | Ge [6] | X |
| 2-n-Propylthiophene | Un [8] | |
| 3-n-Propylthiophene | Ru,[4] As [9] | |
| 2-Isopropylthiophene | Ru,[4] Un,[8] As [9] | X |
| 3-Isopropylthiophene | Un [8] | |
| 2-Methyl-4-ethylthiophene | | X |
| 2,3,5-Trimethylthiophene | | X |
| 2-n-Butylthiophene | Ru,[4] As [9] | |
| 2-Methyl-5-isopropylthiophene | | X |
| 2-Methyl-5-n-propylthiophene | | X |
| 2,3-Dimethyl-5-ethylthiophene | | X |
| 2,4-Dimethyl-5-ethylthiophene | | X |
| 2-Methyl-5-sec-butylthiophene | | X |
| Benzo [b] thiophene | En,[2] Ge [6] | X |
| Ethanethiol (ethyl mercaptan) | Sw [5] | |
| 1-Propanethiol (propyl mercaptan) | Sw [5] | |
| 2-Propanethiol (isopropyl mercaptan) | Sw [5] | |
| 2,3-Dithiabutane (methyl disulfide) | Sw [5] | |
| 2,3,4-Trithiapentane (methyl trisulfide) | Sw [5] | |
| 3,4-Dithiahexane (ethyl disulfide) | Sw [5] | |
| Thiacyclopentane (tetrahydrothiophene) | En,[2] Ru [4] | |
| 2-Methylthiacyclopentane (2-methyltetrahydrothiophene) | | X |

[1] Abbreviations refer to location of origin of shale: En, England, Ru, U.S.S.R., Ge, Germany; As, Austria; Sw, Sweden; Un, Unknown.

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Footnotes for Table 1—Continued

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[23] Horie, F., Composition of Fushun Shale Oil. VII. Olefinic Hydrocarbons Boiling at 50°–85°: Jour. Soc. Chem. Ind., Japan, vol. 38, supp. binding, 1935, pp. 332–334. (Chem. Abs., vol. 29, 1935, p. 6742.)

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[25] Sivertsev, A. P., and Budzko, S., Investigation of the Composition of Gdov Shale Gasoline: Khim. Tverdogo Topliva, vol. 8, 1937, pp. 325–331. (Chem. Abs., vol. 32, 1938, p. 1911.)

[26] Horie, F., Composition of Fushun Shale Oil. XI. Olefin Hydrocarbons Boiling at 115°–133°: Jour. Soc. Chem. Ind., Japan, vol. 38, supp. binding, 1936, pp. 13–14. (Chem. Abs., vol. 30, 1936, p. 3982.)

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[28] Bergh, S., Hydrocarbons in the Gas From Shale Distillation: Tek, Tid., vol. 71, No. 10, Uppl. A–C, Kemi., 1941, pp. 21–24. (Chem. Abs., vol. 36, 1942, p. 5001.)

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TABLE 3.—*Nitrogen-containing compounds identified in shale-oil naphtha*

(X=Identified in this investigation)

| Compound | Previous identification[1] | This investigation |
|---|---|---|
| Pyridine | Sc,[2] Ru[3] | X |
| 2-Methylpyridine | Sc,[2,4] Ru,[3] Ma,[5,6] Co[7] | X |
| 3-Methylpyridine | Ru,[3] Sc,[4] Ma,[6,8] Co[7] | X |
| 4-Methylpyridine | Sc,[4] Ma,[6,8] Co[7] | X |
| 2,3-Dimethylpyridine | Sc,[4,9] Ma,[6,8] Es[10] | X |
| 2,4-Dimethylpyridine | Sc,[2,4] Ru,[3,11] Ma,[5,6] Es[10] | X |
| 2,5-Dimethylpyridine | Sc,[2] Ru,[3] Ma[6,8] | |
| 2,6-Dimethylpyridine | Sc,[2,4] Ru,[3,11] Ma[5,6] | X |
| 3,4-Dimethylpyridine | Sc,[4] Ma[6,8] | X |
| 3,5-Dimethylpyridine | Sc,[4] Ma[6,8] | |
| 2-Ethylpyridine | Ma[6] | |
| 3-Ethylpyridine | Es,[10] Ru[11] | |
| 4-Ethylpyridine | Es[10] | |
| 2,3,5-Trimethylpyridine | Sc,[4] Ma[6,8] | X |
| 2,3,6-Trimethylpyridine | Ma,[6,8] Es[10] | X |
| 2,4,5-Trimethylpyridine | Sc,[4] Ma[6,8] | |
| 2,4,6-Trimethylpyridine | Sc,[2,4] Ma,[5,6] Co,[12,13] Au[14] | X |
| 2-Methyl-4-ethylpyridine | Sc,[4] Ma,[6,8] Ru[11] | X |
| 4-Methyl-2-ethylpyridine | | X |
| 2-Methyl-5-ethylpyridine | Ru,[11] Co[13] | |
| 2-Methyl-6-ethylpyridine | Sc,[4] Ma,[6,8] Ru[11] | |
| 4-Methyl-3-ethylpyridine | Ru[11] | |
| 2,3,4,5-Tetramethylpyridine | Ma[6] | |
| 2,3,4,6-Tetramethylpyridine | Sc,[4] Ma[6,8] | X |
| 2,3,5,6-Tetramethylpyridine | Sc[4] | |
| 2,6-Dimethyl-4-ethylpyridine | Ma[8] | X |
| 2,4-Dimethyl-6-ethylpyridine | | X |
| 2,4-Diethylpyridine | Ru[11] | |
| 2-Butylpyridine | Ru[11] | |
| Quinoline | Ma,[6] Es,[10] Co[15] | X |
| Isoquinoline | Ma,[6] Co[15] | |
| Dihydropyrindine | Ma[8] | |
| Pyrrole | | X |
| 2-Methylpyrrole | | X |
| 2,3,5-Trimethylpyrrole | Ma[16] | |
| 2,3,4,5-Tetramethylpyrrole | | X |
| 2,3.5-Trimethyl-3-ethylpyrrole | | X |
| Benzonitrile | | X |
| 2-Methylbenzonitrile | | X |
| 3-Methylbenzonitrile | | X |
| Hexanenitrile | Ma[17] | |
| Heptanenitrile | Ma[17] | |
| Octanenitrile | Ma[17] | |

previous workers. In general, for the pyridines, compounds in the two columns in the table are similar and include most of the possible homologs having methyl substituents. Several compounds containing an ethyl substituent are included in the list, but, with one exception, no compound with a substituent group larger than ethyl has been identified. These results are similar to those obtained for aromatic hydrocarbons and thiophenes, which indicates the scarcity of compounds with a single alkyl substituent larger than methyl. Two of the compounds, 4-methyl-2-ethylpyridine and 2,4-dimethyl-6-ethylpyridine, identified in this study have not been reported previously from shale-oil sources. At the time of its identification in this investigation, the latter compound apparently had not appeared previously in the chemical literature. The presence of pyrroles as a class has been observed by many investigators. However, the pyrroles and nitriles from Colorado shale oil were the first individual compounds reported as having been identified. Soon after this the presence of 2,3,5-trimethylpyrrole in Fushun shale oil was reported.

The oxygen compounds identified in shale-oil naphthas are both acidic and nonacidic. The acidic compounds are chiefly phenols with much smaller quantities of carboxylic acids. The nonacidic compounds are heterocyclics, alcohols, ketones, and ethers. The compounds identified are listed in table 4. For the phenols, the only group in which a substantial number of compounds was identified, the table contains all the homologs boiling below about 220° C., but none boiling above this temperature. This situation apparently occurs because the naphthas are usually prepared by distillation to a cut temperature of 200° C. so that the presence of compounds with boiling points above this temperature is due to poor fractionation. Since nearly all of the phenols shown in table 4 boil above 200° C., the quantity present decreases with increase in boiling point so that compounds boiling above 220° C. were present in too small a quantity for ready identification. The increased difficulty of identifying higher boiling homologs may also be a contributing factor.

## COMPOUND DISTRIBUTION

The identification of individual compounds, as discussed in the preceding section, gives information as to general characteristics of shale oil. For example, it establishes that certain types of compounds, such as benzenes with a single alkyl substituent larger than propyl, were not present in the Colorado shale-oil naphthas examined in sufficient quantities to be identified. However, variations in shale

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[1] Abbreviations refer to location of origin of shale; Co, Colorado; Ma, Manchuria; Sc, Scotland; Ru, U.S.S.R.; Au, Australia.

[2] Garrett, F. C., and Smythe, J, A., The Bases Contained in Scottish Shale Oil, Part I: Jour. Chem. Soc. (London), vol. 81, 1902, pp. 449–456.

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[8] Eguchi, T., Basic Nitrogen Compounds From Fushun Shale Tar. II: Bull. Chem. Soc., Japan, vol. 3, 1928, pp. 227–243. (Brit. Abs., 1929, B. p. 6.)

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[14] Cane, R. F., The N. Bases in Tasmanite Shale Oil: Papers and Proc. Roy. Soc. Tasmania, 1941, pp. 55–62. (Chem. Abs., vol. 38, 1944, p. 635.)

[15] Lochte, H. M., and Meyer, H. W. N., Some Colorado Shale-Oil Bases: Jour. Am. Chem. Soc., vol. 78, 1956, pp. 2150–2153.

[16] Iida, T., Components of Fushun Shale Oil. II. 2,3,5-Trimethylpyrrole From Crude Gasoline: Pharm. Bull. (Japan), vol. 1, 1953, pp. 209–211. (Chem. Abs., vol. 48, 1954, p. 11034.)

[17] Iida, T., and Tanka, M., Constituents of Fushun Shale Oil. I. Nitrile Compounds in Naphtha: Jour. Pharm. Soc. (Japan), vol. 64, No. 9A, 1944, pp. 33–34. (Chem. Abs., vol. 45, 1951, p. 3583.)

TABLE 4.—*Oxygen-containing compounds identified in shale-oil naphtha*

(X=Identified in this investigation)

| Compound | Previous identification [1] | This investigation |
|---|---|---|
| Phenol | Co,[2] Es,[3, 4] Sc,[5] Sw [6] | X |
| 2-Methylphenol | Es,[3, 7] Sc,[5] Ru [8–11] | X |
| 3-Methylphenol | Es,[3, 7] Sc,[5] Ru,[8–11] Sw,[12] Ta [13]. | X |
| 4-Methylphenol | Es,[3, 7] Ru,[8–11] Sw [12] | X |
| 2,3-Dimethylphenol | Es [3] | X |
| 2,4-Dimethylphenol | Es,[7] Ru [8, 9, 11] | X |
| 2,5-Dimethylphenol | Es,[3, 7] Ru [8, 9] | X |
| 2,6-Dimethylphenol | | X |
| 3,4-Dimethylphenol | Sc,[5] Es,[7, 14] Ru [8, 9] | X |
| 3,5-Dimethylphenol | Sc,[5] Ru,[9, 11, 15] Es [14] | X |
| 2-Ethylphenol | | X |
| 3-Ethylphenol | Es,[3] Ru [9, 11] | |
| 4-Ethylphenol | Ru [8, 9] | X |
| 2,4,6-Trimethylphenol | | X |
| Butanoic acid | Es [16] | |
| Pentanoic acid | Es [16] | |
| Hexanoic acid | Es [16] | |
| Heptanoic acid | Es [16] | X |
| Octanoic acid | Es [16] | |
| Benzoic acid | | X |
| Benzofuran | | X |
| Ethanol | Ru [17] | |
| 2-Propanone | Sw [6, 12, 18] | |
| 2-Butanone | Sw [6, 12] | |
| 2-Pentanone | Sw [12] | |
| 3-Pentanone | Sw [6] | |
| 2-Heptanone | Es [19] | |
| 2-Octanone | Es [19] | |
| 2-Nonanone | Es [19] | |
| 2-Decanone | Es [19] | |
| 2,4-Dimethylcyclohexanone | Es [19] | |
| Isopropyl ether | Ru [17] | |

[1] Abbreviations refer to locations of origin of shale: Co, Colorado; Es, Estonia; Ru, U.S.S.R.; Sc, Scotland; Sw, Sweden; Ta, Tasmania.

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[3] Raudsepp, Kh. T., Individual Compounds and Total Phenols of Schist Tar: Trudy Tallin. Politekh. Inst., No. 63A., 1955, pp. 90–115; Referat. Zhur. Khim., 1956, abs., No. 59101. (Chem. Abs., vol. 53, 1959, p. 4701.)

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[5] Gray, T., The Phenols From Shale Oil: Jour. Soc. Chem. Ind., vol. 21, 1902, p. 845.

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[8] Broun, A. S., and Tseitlin, A. S., Acidic Fractions of Tar From Gdov Bituminous Shale: Khim. Tverdogo Topliva, vol. 7, 1936, pp. 136–143. (Chem. Abs., vol. 31, 1937, p. 2798.)

[9] Broun, A. S., Zelenina, E. M., and Sukacheva, T. V., The High Temperature Tar of Gdov Shale: Khim. Tverdogo Topliva, vol. 5, 1934, pp. 771–787. (Chem. Abs., vol. 29, 1935, p. 7632.)

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[13] Cane, R. F., Tasmanite Shale Oil: Papers and Proc. Royal Soc., Tasmania, 1941, pp. 23–32. (Chem. Abs., vol. 38, 1944, p. 241.)

[14] Raudsepp, Kh. T.: Goryuchie Slantsy-Khimiya i Tekhnologiya, No. 2, Tallinn, 1956, pp. 107–116. (Kirss, V., The Research on the Estonian Oil Shale After the World War II: Yearbook of the Estonian Learned Society in America, vol. 2, 1954–1958, pp. 7–42.)

[15] Andreevskii, D. N., and Chegis, A. F., The Composition of the Acidic Fractions of the Tars From Petrograd Shales: Khim Tverdogo Topliva, vol. 4, 1933, pp. 469–480. (Chem. Abs., vol. 28, 1934, p. 6280.)

[16] Valdek, R. K., Izvest. Akad. Nauk. Eston. S.S.R., vol. 2, 1953, pp. 235–251. (Kirss, V., The Research on the Estonian Oil Shale After the World War II: Yearbook of the Estonian Learned Society in America, vol. 2, 1954–1958, pp. 7–42.)

[17] Gerasimov, M. M., and Glushnev, V. E., Cracking of Tar (Freed From Gasoline) From the Gdov Deposit Shales: Bull. Acad. Sci. U S. S.R., Classe Sci. Tech., vol. 4, 1940, pp. 29–35. (Chem. Abs., vol. 36, 1942, p. 1170.)

[18] Hellsing, G., Contribution to the Knowledge of the Composition of Swedish Shale Oil: Arkiv Kemi, Mineral Geol., Stockholm, vol. 7, No. 29, 1921, 23 pp. (Chem. Abs., vol. 15, 1921, p. 3552.)

[19] Semenov, S. S., and Gurwich, B. E., Investigation of Neutral Oxygen Compounds From Shale Tar Fractions: Trudy Vsesoyuznogo Nauchno-Issledovotelskogo Instituta po Pererabotke Slantsev, No. 2, 1954, pp. 57–68.

source and in conditions of oil production are apt to change the relative quantities of compounds present. Hence, the quantitative distribution of compounds, a subject on which there is relatively little information in the literature, is an important phase of composition studies.

In the present investigation several primary naphthas and one thermally cracked naphtha were analyzed in sufficient detail to furnish distribution data on individual compounds or related groups of compounds. In addition a number of other naphthas and gasolines were analyzed for their content of various types of compounds.

## PRIMARY NAPHTHAS

### DETAILED COMPARISONS

The compositions of the hydrocarbon portions of three primary naphthas from Colorado shale oil and one from Scottish shale oil are given in table 5. The Colorado naphthas are designated by the name of the retort—Pumpherston,[28] N-T-U,[28] or high temperature [29]—that was used to obtain the oil from which they were distilled. Data on the Scottish oil [30] represent the only comprehensive work reported in the literature on a single oil other than those from Colorado shale. Direct comparison of results on the four naphthas is difficult for several reasons: Results on the Colorado naphthas are reported on a volume basis, whereas those on the Scottish naphtha are on a weight basis; Haresnape and Lowry did their work on a light naphtha, boiling up to 150° C., so that only compounds containing eight carbon atoms or less were determined; and resolution of the saturate and olefin portions of the 1,200° F. naphtha was not as complete as for the other naphthas because the analysis was made for comparison with other high-temperature naphthas in a study in which the distribution of aromatics was of primary interest. In spite of these difficulties some trends in composition can be observed. The naphtha from oil produced at 1,200° F. differs substantially from the other three naphthas. The relative quantity of compounds in the $C_5$-to-$C_8$ region is high for this naphtha. In this region the 1,200° F. naphtha has a much higher proportion of cyclic compounds than the other naphthas. These differences may be due partly to more efficient recovery of material in this boiling range, but

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[28] Cattell, R. A., Guthrie, Boyd, and Schramm, L. S., Retorting Colorado Oil Shale—A Review of the Work of the Bureau of Mines, U.S. Department of the Interior: Oil Shale and Cannel Coal, vol. 2, Inst. Petrol., London, 1951, pp. 345–398.

[29] Brantley, F. E., Cox, R. J., Sohns, H. W., Barnet, W. I., and Murphy, W.I.R., High Temperature Shale Oil, Production and Utilization: Ind. Eng. Chem., vol. 44, 1952, pp. 2641–2647.

[30] Haresnape, D., and Lowry, R. A., The Chemical Composition of Scottish Shale Oil Distillates: Oil Shale and Cannel Coal, 2d conf., vol. 2, Inst. Petrol., London, 1951, pp. 727–740.

TABLE 5.—*Quantities of hydrocarbons found in shale-oil naphthas*

| Compound | Results expressed as amount in crude oil from | | | |
|---|---|---|---|---|
| | Scotland by Pumpherston retort, wt.-pct. | Colorado by Pumpherston retort, vol.-pct. | Colorado by N–T–U retort, vol.-pct. | Colorado by 1,200° F. high-temperature retorting, vol.-pct. |
| Paraffins: | | | | |
| n-Pentane | 0. 27 | ---------- | 0. 09 | 0. 16 |
| Isopentane | . 03 | ---------- | | |
| n-Hexane | . 64 | 0. 02 | . 03 | . 28 |
| 2-Methylpentane | . 06 | ---------- | . 02 | |
| 3-Methylpentane | . 03 | ---------- | | |
| n-Heptane | . 76 | . 04 | . 04 | . 65 |
| 3-Methylhexane | . 04 | . 04 | . 03 | |
| Other $C_7$-paraffins | . 07 | | | |
| n-Octane | . 71 | . 30 | . 09 | . 29 |
| 2-Methylheptane | . 07 | . 04 | . 05 | |
| 3-Methylheptane | . 05 | | | |
| 4-Methylheptane | . 02 | | | |
| Dimethylhexanes | ---------- | . 06 | | |
| n-Nonane | ---------- | . 64 | . 09 | . 43 |
| Methyloctanes | . 05 | . 09 | . 11 | |
| Dimethylheptanes | ---------- | . 11 | | |
| n-Decane | ---------- | . 77 | . 32 | . 90 |
| Methylnonanes | ---------- | . 09 | . 11 | |
| Other $C_{10}$-paraffins | ---------- | . 32 | | |
| n-Undecane | ---------- | ---------- | . 34 | . 17 |
| Other $C_{11}$-paraffins | ---------- | ---------- | . 12 | |
| Cycloparaffins: | | | | |
| Cyclopentane | . 04 | ---------- | ---------- | . 79 |
| Cyclohexane | . 06 | . 01 | Trace | . 26 |
| Methylcyclopentane | . 06 | | | |
| Methylcyclohexane | . 08 | . 01 | . 02 | 1. 18 |
| Ethylcyclopentane | . 06 | . 01 | | |
| Dimethylcyclopentanes | ---------- | ---------- | | |
| Ethylcyclohexane | . 07 | ---------- | . 03 | . 58 |
| Dimethylcyclohexanes | . 09 | . 13 | | |
| n-Propylcyclopentane | . 01 | ---------- | | |
| 1,2,4-Trimethylcyclopentane | ---------- | . 02 | | |
| $C_9$-cycloparaffins | . 05 | . 40 | . 09 | . 04 |
| $C_{10}$-cycloparaffins | ---------- | . 30 | . 12 | . 02 |
| $C_{11}$-cycloparaffins | ---------- | ---------- | . 11 | . 02 |
| $C_{12}$-cycloparaffins | ---------- | ---------- | . 03 | . 03 |
| Aliphatic olefins: | | | | |
| Butenes | ---------- | ---------- | ---------- | . 42 |
| 1-Pentene | . 10 | ---------- | . 08 | 1. 59 |
| 2-Pentene | . 09 | ---------- | | |
| Trimethylethylene | . 03 | ---------- | | |
| 1-Hexene | . 42 | ---------- | . 04 | . 14 |
| 2- and 3-Hexene | . 27 | ---------- | | |
| 1-Heptene | . 35 | . 13 | . 03 | . 37 |
| 2-Heptene | . 19 | | | |
| 3-Heptene | . 11 | | | |
| Other $C_7$-olefins | . 03 | | . 04 | |
| 1-Octene | . 30 | . 47 | . 10 | 1. 49 |
| 2-Octene | . 13 | | | |
| 3- and 4-Octene | . 07 | | | |
| Other $C_8$-olefins | . 23 | | . 01 | |
| n-Nonenes | ---------- | . 79 | . 18 | 1. 07 |
| Other $C_9$-olefins | ---------- | . 21 | . 11 | |
| n-Decenes | ---------- | . 81 | . 24 | . 67 |
| Other $C_{10}$-olefins | ---------- | . 36 | . 16 | |
| n-Undecenes | ---------- | ---------- | . 29 | . 32 |
| Other $C_{11}$-olefins | ---------- | ---------- | . 29 | |
| n-Dodecenes | ---------- | ---------- | . 06 | . 38 |
| Other $C_{12}$-olefins | ---------- | ---------- | . 17 | |

TABLE 5.—*Quantities of hydrocarbons found in shale-oil naphthas*—Continued

| Compound | Results expressed as amount in crude oil from | | | |
|---|---|---|---|---|
| | Scotland by Pumpherston retort, wt.-pct. | Colorado by Pumpherston retort, vol.-pct. | Colorado by N-T-U retort, vol.-pct. | Colorado by 1,200° F. high-temperature retorting, vol.-pct. |
| Cyclic olefins and diolefins: | | | | |
| Butadiene | ------ | ------ | ------ | 0. 25 |
| Cyclopentene | 0. 03 | ------ | ------ | 1. 95 |
| Pentadienes | ------ | ------ | ------ | |
| Cyclopentadiene | ------ | ------ | ------ | . 39 |
| Cyclohexene | ------ | 0. 03 | 0. 02 | . 61 |
| Methylcyclopentene | . 03 | | | |
| Dimethylcyclopentenes | . 07 | . 09 | . 05 | . 68 |
| Other $C_7$-cyclic olefins | . 08 | | | |
| $C_8$-cyclic olefins | . 15 | . 26 | . 12 | . 37 |
| $C_9$-cyclic olefins | ------ | . 60 | . 13 | . 58 |
| $C_{10}$-cyclic olefins | ------ | . 49 | . 20 | . 22 |
| $C_{11}$-cyclic olefins | ------ | ------ | . 12 | . 10 |
| $C_{12}$-cyclic olefins | ------ | ------ | . 07 | . 23 |
| Aromatics: | | | | |
| Benzene | . 20 | . 04 | . 01 | 4. 88 |
| Toluene | . 27 | . 21 | . 02 | 4. 41 |
| Ethylbenzene | . 16 | . 06 | . 02 | 2. 11 |
| p-Xylene | . 03 | . 13 | . 01 | |
| m-Xylene | . 08 | . 30 | . 06 | |
| o-Xylene | . 05 | . 17 | . 02 | |
| Styrene | ------ | ------ | Trace | . 52 |
| Isopropylbenzene | ------ | ------ | . 01 | 1. 09 |
| n-Propylbenzene | ------ | ------ | . 01 | |
| 1-Methyl-3-ethylbenzene | ------ | . 15 | Trace | |
| 1-Methyl-4-ethylbenzene | ------ | . 08 | . 06 | |
| 1-Methyl-2-ethylbenzene | ------ | . 17 | . 02 | |
| 1,3,5-Trimethylbenzene | ------ | | | |
| 1,2,4-Trimethylbenzene | ------ | . 28 | . 06 | . 19 |
| tert-Butylbenzene | ------ | | | |
| sec-Butylbenzene | ------ | | | |
| iso-Butylbenzene | ------ | | | |
| 1,2,3-Trimethylbenzene | ------ | . 34 | . 15 | |
| 1-Methyl-2-isopropylbenzene | ------ | | | |
| 1-Methyl-3-isopropylbenzene | ------ | | | |
| 1-Methyl-4-isopropylbenzene | ------ | | | |
| 1,3-Diethylbenzene | ------ | ------ | . 02 | |
| 1,4-Diethylbenzene | ------ | ------ | . 06 | |
| Other $C_{10}$-alkylbenzenes | ------ | ------ | . 05 | |
| $C_{11}$-alkylbenzenes | ------ | ------ | . 16 | . 67 |
| Indene | ------ | ------ | ------ | . 80 |
| Naphthalene | ------ | ------ | Trace | . 47 |

the major cause seems to be the higher temperature of production, which would be expected to produce lower boiling, unsaturated, cyclic compounds. The other three naphthas have similarities of composition in spite of differences in boiling range.

The relationships among straight-chain, branched-chain, and cyclic compounds in the saturates and olefins from N-T-U naphtha are illustrated in figure 2. For the olefins the three classes of compounds are present in about equal quantities, whereas for the saturates the proportions are about: 3 parts straight-chain compounds, 2 parts branched-chain compounds, and 1 part cyclic compounds. The N-T-U naphtha contains some of each molecular-weight group (about 5 to 12 carbon atoms per molecule) usually found in a gasoline, but has a preponderance of material in the 10- and 11-carbon-atom range. This distribution, which is shown in figure 3 for saturates and olefins, may be partly due to failure of the retort condensing system to recover lower boiling compounds. Illustrative of the distribution is the fact that two compounds, n-decane and n-undecane, amount to one-third of the total saturates.

The distribution of the aromatics by molecular-weight groups (through the $C_9$-benzenes) for the three Colorado naphthas is shown in

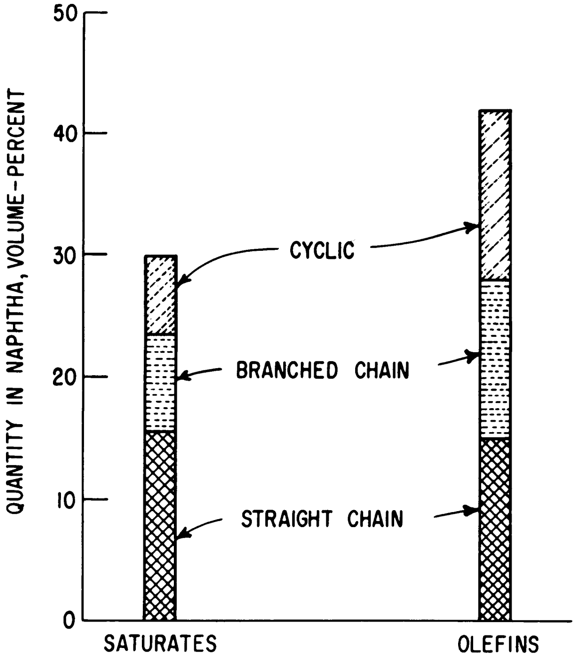

FIGURE 2.—Distribution of Types of Compounds in Saturates and Olefins From N–T–U Primary Naphtha.

figure 4, together with data for three additional naphthas. The N–T–U and Pumpherston naphthas are similar but differ from the others, which show more lower boiling compounds. This trend is possibly correlated with increases in retorting temperature.

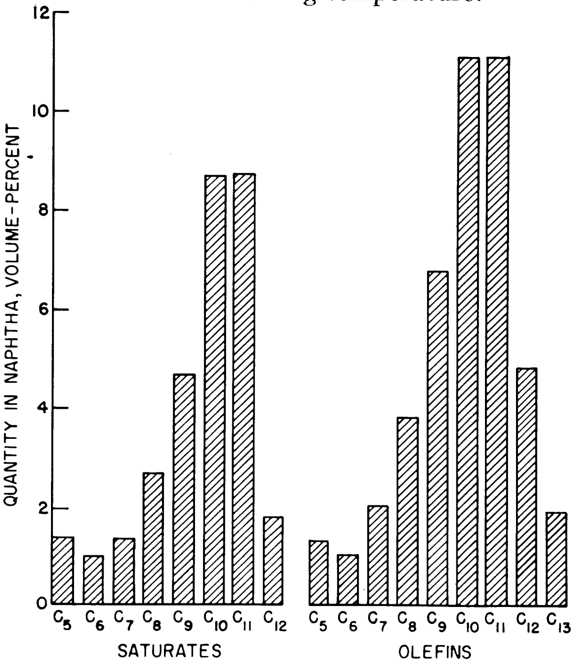

FIGURE 3.—Molecular-Weight Distribution of Saturates and Olefins in N–T–U Primary Naphtha.

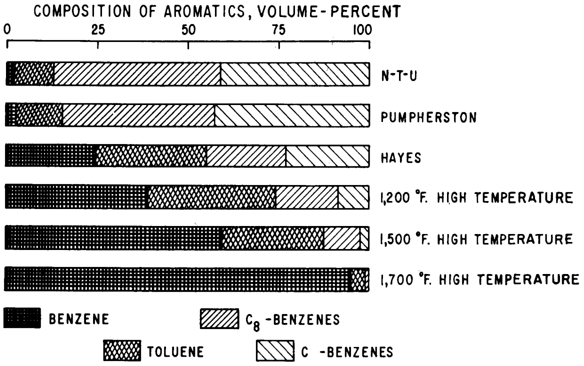

FIGURE 4.—Distribution of Aromatic Hydrocarbons in Various Colorado Shale-Oil Naphthas.

Figure 5 shows quantitative estimates for the 18 thiophenes identified in N–T–U naphtha. The sulfur in the 18 thiophenes represents over two-thirds of the thiophenic sulfur, or about one-half of the total sulfur, in the naphtha. As there are over 120 homologs of thiophene boiling in the range of the naphtha, the 18 thiophenes identified would account on a statistical basis for only 15 pct. of the thiophenic sulfur rather than for the nearly 70 pct. that they actually do. This emphasizes the fact, shown previously for the alkyl benzenes, that certain substitution patterns are favored by the reactions taking place during retorting.

The quantitative estimates indicate a definite substitution pattern for these lower boiling compounds: 2-Monosubstitution predominates over 3-monosubstitution; 2,5-disub-

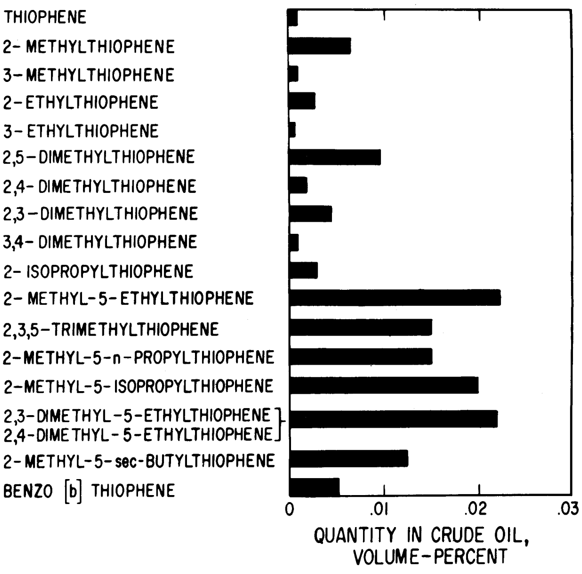

FIGURE 5.—Estimated Amounts of Thiophenes in N–T–U Shale Oil.

stitution predominates over the other types of disubstitution; and 2,3,5-trisubstitution predominates over 2,3,4-trisubstitution. For example, appreciable 2,3,5-trimethylthiophene was present, but 2,3,4-trimethylthiophene was not present in sufficient quantity to be isolated by the techniques used. In an homologous series such as 2-monoalkylthiophenes, the quantity of the compound decreases as the length of the alkyl substituent increases. This is the same trend that was observed for the aromatic hydrocarbons.

2-Methylthiophene, 2,5-dimethylthiophene, 2-methyl-5-ethylthiophene, and 2-methyl-5-isopropylthiophene are the predominant isomers in their respective molecular-weight groups. The abundance of the latter two compounds in particular suggests a tendency for the predominant isomer in a molecular-weight group to have a methyl group in the 2-position plus another group of increased size rather than a single group or two groups of similar size. For example, 2-methyl-5-isopropylthiophene was present, but butylthiophene and diethylthiophene were not found.

Figure 6 gives an estimate of the contents of the individual pyridines identified in the N–T–U naphtha. These estimates were made from the distillation curve of the pyridine bases. Plateaus on the curve were apportioned among the components identified in individual fractions. The values obtained by this technique are only an order-of-magnitude estimate, but they give some idea of the relative abundance of the compounds. A preponderance of compounds substituted in the 2,4,6-positions is shown.

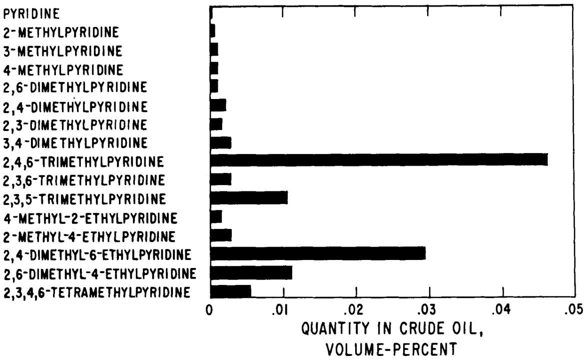

FIGURE 6.—Estimated Amounts of Pyridines in N–T–U Shale Oil.

TABLE 6.—*Composition of phenols extracted from shale-oil naphthas*

| Compound | Results expressed as volume-percent in crude oil from | | |
|---|---|---|---|
| | N–T–U retort | 1,200°F. high-temperature retort | 1,500° F. high-temperature retort |
| Phenol | 0.010 | 0.007 | 0.105 |
| 2-Methylphenol | .018 | .021 | .066 |
| 3-Methylphenol | .010 | .021 | .057 |
| 4-Methylphenol | .017 | ---------- | ---------- |
| 2-Ethylphenol | .001 | .007 | .006 |
| 4-Ethylphenol | .001 | ---------- | ---------- |
| 2,3-Dimethylphenol | .004 | .021 | .009 |
| 2,4-Dimethylphenol | .007 | .105 | .033 |
| 2,5-Dimethylphenol | .003 | ---------- | .009 |
| 2,6-Dimethylphenol | .005 | ---------- | ---------- |
| 3,4-Dimethylphenol | ---------- | .014 | ---------- |
| 3,5-Dimethylphenol | ---------- | .028 | ---------- |
| 2,4,6-Trimethylphenol | Trace | ---------- | ---------- |

The amounts of phenols in three shale oils—one from an N–T–U retort and two from high-temperature retorting—are shown in table 6. The results in table 6 should be compared with caution because of the circumstances under which they were obtained. The values for the N–T–U oil do not represent the total quantities of some of the compounds in the crude oil because of the 200° C. cut temperature of the naphtha. The phenols from the high-temperature oils, on the other hand, were extracted from distillates with higher end points so that the values in table 6 should represent the total quantities of the compounds in the oils. However, the quantities of these extracts that were available for study were so small that only the major components could be determined. The results show the presence of larger quantities of the lower boiling homologs as the temperature of retorting increases.

## GENERAL COMPARISONS

Extensive investigations, such as those reported in the preceding discussion, were made on only a limited number of samples. However, the simple analysis of the naphtha fraction obtained in the Bureau of Mines Crude Shale Oil Analysis Procedure [31] yields results useful in showing the effects of retorting variables on naphtha composition. This analysis gives values for tar acids, tar bases, hydrocarbon groups, and nitrogen content in the naphtha. In some cases the sulfur content was also determined.

### NAPHTHAS FROM COLORADO SHALE OILS

Although many methods for retorting shale have been suggested, they have been grouped into four classes [32] according to the method of heat transfer utilized. Retorts representing three of these classes have been used on Colorado shale to produce the oils from which the naphthas to be discussed in this section were obtained. Class I retorts, in which heat is transferred to the shale through a wall, are represented by

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[31] Stevens, R. F., Dinneen, G. U., and Ball, John S., Analysis of Crude Shale Oil: Bureau of Mines Rept. of Investigations 4898, 1952, 20 pp.

[32] Work cited in footnote 28, p. 9.

TABLE 7.—*Analyses of naphthas from Colorado shale oils*

| Retort | Naphtha in crude oil, vol.-pct. | Saturates, neutral naphtha, vol.-pct. | Olefins, neutral naphtha, vol.-pct. | Aromatics, neutral naphtha, vol.-pct. | Sulfur, wt.-pct. | Nitrogen, wt.-pct. |
|---|---|---|---|---|---|---|
| N-T-U | 6. 5 | 34 | 45 | 21 | 1. 24 | 1. 21 |
| Gas combustion | 4. 4 | 27 | 51 | 22 | 1. 03 | 1. 17 |
| Gas flow | 1. 5 | 27 | 42 | 31 | . 71 | 1. 30 |
| Fischer assay | 13. 7 | 33 | 56 | 11 | ---------- | . 74 |
| Pumpherston | 17. 6 | 32 | 43 | 25 | . 84 | . 51 |
| Parry | 14. 9 | 27 | 48 | 25 | . 89 | . 51 |
| Hayes | 27. 7 | 4 | 12 | 84 | ---------- | ---------- |
| 1,200° F. high temperature | 39. 2 | 10 | 39 | 51 | . 79 | . 97 |
| 1,500° F. high temperature | 38. 4 | 1 | 1 | 98 | . 75 | 1. 30 |

Pumpherston,[33] Parry,[34] Hayes,[35] Fischer assay,[36] and high-temperature[37] retorts. The last retort differs from the others in this class in that it is designed to permit heating fine shale rapidly to a controlled temperature higher than normally employed. Class II retorts, in which heat is transferred to the shale from combustion gases generated in the retort, are represented by the N-T-U[38] and gas combustion retorts.[39] Class III retorts, in which heat is transferred to the shale by passing previously heated gases through the shale bed, are represented by the gas flow retort.[40]

Analytical results on naphthas from oils produced in these retorts are given in table 7. The yield of naphtha is lower for the three oils produced in class II and III retorts, which have a sweep gas passing through the shale bed. This is apparently due to minimizing secondary cracking reactions in the retort but may be influenced by the fact that condensing light ends is more difficult in these classes of retorts. The hydrocarbon compositions of the first six naphthas are fairly similar, particularly with respect to the content of saturates. Each class of retort is represented in this group. The last three naphthas, which are substantially less saturated and more aromatic than the first six, are from oils produced at appreciably higher temperatures than the others. Therefore, it seems that the hydrocarbon composition is affected more by the temperature of operation than by the method of heating. The Hayes retort was not designed for high-temperature operation, but in the short experimental runs made with this retort, poor control resulted in some oils being produced at high temperatures. The sulfur and nitrogen values given in table 7 do not show the same division into two groups that the hydrocarbon results do. Although there is a rather large variation among the results shown, they are not readily correlated with retorting methods or operating variables.

The preceding data indicate some of the effects of retorting on naphtha composition. Retorting can have a pronounced effect on composition, particularly if the temperatures employed are much higher than those considered standard practice. However, it seems unlikely that retorts belonging to classes II and III, in which the gases used for heating tend to remove the oil before it attains high temperatures, will produce naphthas differing substantially in composition from those discussed. The naphthas produced at higher temperatures differ from the others both with regard to the relative amouts of the groups of hydrocarbons present (table 7) and with regard to distribution of individual compounds within these groups as shown previously in figure 4. The naphthas are more aromatic as the temperature is increased and the compound distribution is shifted toward the presence of greater relative quantities of the simpler members of the homologous series.

### NAPHTHAS FROM OILS PRODUCED FROM OTHER SHALES

The yields and compositions of naphthas from oils produced from shales found in seven foreign countries and from Tennessee shale in the United States are given in table 8. The hydrocarbon compositions of the naphthas range from those that are decidedly saturated to those containing over 50 pct. aromatics. This variation may result largely from differing characteristics of the shales because results in the preceding section showed that extraordinary retorting conditions were required to show an appreciable effect on composition. This comparative effect is illustrated by the results in fig-

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[33] Work cited in footnote 28, p. 9.

[34] Parry, V. F., Gernes, D. C., Goodman, J. B., Wagner, E. O., Koth, A. W., Patty, W. L., and Yeager, E. O., Gasification of Lignite and Subbituminous Coal Progress Report for 1944: Bureau of Mines Rept. of Investigations 3901, 1946, 59 pp.

[35] Work cited in footnote 28, p. 9.

[36] Stanfield, K. E., and Frost, I. C., Method of Assaying Oil Shale by a Modified Fischer Retort: Bureau of Mines Rept. of Investigations 4477, 1949, 13 pp.

[37] Work cited in footnote 29, p. 9.

[38] Work cited in footnote 28, p. 9.

[39] Cameron, R. J., and Guthrie, Boyd, Oil From Shale: Chem. Eng. Prog., vol. 50, 1954, pp. 336–341.

[40] Work cited in footnote 28, p. 9.

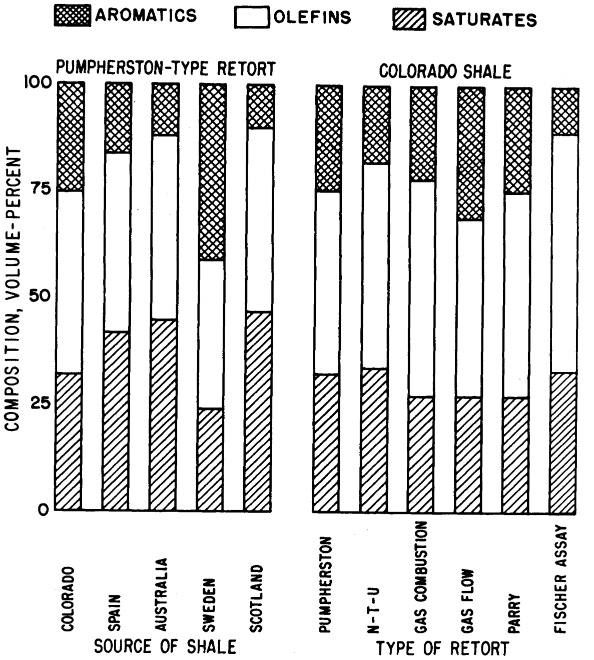

FIGURE 7.—Comparison of the Hydrocarbon Composition of Naphthas From Foreign and Colorado Shale Oils.

ure 7. The five naphthas in the set on the left in the figure were obtained from shales from different countries using Pumpherston-type retorts. The differences in composition of these naphthas, which should result mainly from effects of shale characteristics, are greater than the differences among the six naphthas on the right, which should result mainly from the retorting method.

The effect of shale characteristics on composition is also indicated by the values for sulfur and nitrogen in table 8. The nitrogen content of the Brazilian naphtha is similar to those for the Colorado naphthas and is substantially higher than those for the rest of the foreign naphthas. These results appear to be essentially independent of retorting method. The average nitrogen content of the Brazilian and Colorado naphthas is about 5 times that of the other naphthas, although the nitrogen content of the organic matter in the shales from which they came is only twice the average of the other shales. The lower nitrogen values obtained on many of the naphthas are reflected in the low tar-base contents shown in table 8. The sulfur values for the naphthas do not fall into the same groups as do the nitrogen values. Sulfur contents of the Colorado naphthas (table 7) show relatively minor variations, and all come within the range of values, 0.27 to 3.17, shown in table 8.

## CRACKED NAPHTHAS

Most Colorado crude shale oils contain only small quantities of primary naphtha, so cracking processes usually are required to produce appreciable quantities of gasoline. Several naphthas resulting from thermal

TABLE 8.—*Analyses of naphthas from various shale oils*

| Source and retort | Naphtha in crude oil, vol.-pct. | Composition of naphtha | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Tar acids, vol.-pct. | Tar bases, vol.-pct. | Neutral naphtha, vol.-pct. | | | Sulfur, wt.-pct. | Nitrogen, wt.-pct. |
| | | | | Saturates | Olefins | Aromatics | | |
| Tennessee: | | | | | | | | |
| Royster-T.V.A | 6. 0 | 3. 2 | 1. 6 | 25 | 21 | 54 | 2. 34 | 0. 22 |
| Spain: | | | | | | | | |
| Pumpherston | 13. 8 | 1. 7 | 1. 0 | 42 | 42 | 16 | . 27 | . 18 |
| South Africa: | | | | | | | | |
| Salermo | 19. 1 | 1. 8 | . 6 | 37 | 48 | 15 | . 43 | . 14 |
| Australia: | | | | | | | | |
| Pumpherston | 14. 6 | 1. 4 | 2. 3 | 45 | 43 | 12 | . 41 | . 10 |
| Sweden: | | | | | | | | |
| Rockesholm | 16. 5 | 2. 2 | . 7 | 24 | 35 | 41 | 1. 42 | . 17 |
| Ljungstrom | 76. 8 | . 4 | . 2 | 63 | 11 | 26 | . 70 | . 07 |
| Scotland: | | | | | | | | |
| Pumpherston | 19. 5 | 1. 2 | . 8 | 47 | 43 | 10 | . 27 | . 13 |
| France: | | | | | | | | |
| Pumpherston | 2. 3 | --- | --- | --- | --- | --- | . 42 | . 40 |
| Marecaux | 23. 5 | 1. 6 | . 4 | 31 | 41 | 28 | 3. 17 | . 15 |
| Cantieny | 27. 9 | 1. 2 | 1. 2 | 25 | 22 | 53 | 2. 94 | . 16 |
| Lantz | 19. 7 | 2. 0 | 2. 0 | 37 | 47 | 16 | . 50 | . 11 |
| Brazil (Paraiba Valley): | | | | | | | | |
| Fischer assay | 16. 4 | 2. 7 | 6. 4 | 19 | 60 | 21 | --- | 1. 17 |

cracking of N–T–U stocks were analyzed for hydrocarbon-group composition. Four of the naphthas were from once-through operations and were similar in composition to each other and to the primary naphthas from conventional retorting. This is illustrated in table 9, which gives the average composition of the first six naphthas from table 7 and the four cracked naphthas. The other naphtha in table 9 was from recycle cracking and has nearly twice as high a content of saturates, half the quantity of olefins, and about the same amount of aromatics as the other naphthas. Because of the difference in composition of the recycle-cracked naphtha, it was subjected to a more detailed analysis, and the results were compared with those obtained on the primary N–T–U naphtha.

The relative distribution of saturates and olefins for the recycle and primary naphthas is shown in table 10. There is a difference in the boiling-range distributions of the samples. The primary naphtha contains a wider range of molecular-weight groups than does the cracked naphtha, but has a less even distribution as there is a greater relative concentration in the $C_{10}$ and $C_{11}$ groups. Although the cracked naphtha has twice the content of saturates that is present in the primary naphtha, the distribution of compound types shows similarities for the two naphthas. Paraffins compose 72 pct. of the saturates in the cracked naphtha as compared to 79 pct. in the primary naphtha. Of these paraffins, 63 pct. are normal compounds in each of the naphthas. In the case of the olefins, aliphatic compounds make up 63 pct. of the total for the cracked naphtha and 69 pct. for the primary naphtha.

A comparison of the individual aromatic compounds determined in the two naphthas is given in table 11. The total quantity of aromatics in the two naphthas is about the same and, as shown in table 11, the distribution is similar. Also, the naphthas show the presence and absence of the same aromatic compounds. For example, in the group consisting of tert-butylbenzene, 1,2,4-trimethylbenzene, isobutylbenzene, and sec-butylbenzene, which have boiling points so close together that separation by distillation is difficult, ultraviolet and mass spectra indicated the presence of 1,2,4-trimethylbenzene as the predominant compound in each of the naphthas.

Table 9.—*Hydrocarbon composition of primary and cracked naphthas, in volume-percent*

| Type of naphtha | Number of samples averaged to obtain reported results | Saturates | Olefins | Aromatics |
|---|---|---|---|---|
| Primary | 6 | 30 | 48 | 22 |
| Single pass cracked | 4 | 30 | 55 | 15 |
| Recycle cracked | 1 | 55 | 25 | 20 |

Table 10.—*Distribution of saturates and olefins in primary and cracked shale-oil naphthas, in volume-percent*

| Molecular-weight group | Saturates | | Olefins | |
|---|---|---|---|---|
| | N–T–U primary naphtha | Recycle-cracked naphtha | N–T–U primary naphtha | Recycle-cracked naphtha |
| Aliphatics: | | | | |
| $C_5$ | 4.9 | | 3.5 | |
| n-$C_6$ | 2.0 | | 1.9 | |
| Other $C_6$ | 1.4 | | | |
| n-$C_7$ | 2.1 | 2.1 | 1.5 | 2.0 |
| Other $C_7$ | 1.5 | 1.9 | 1.9 | 2.6 |
| n-$C_8$ | 4.9 | 8.3 | 4.5 | 8.4 |
| Other $C_8$ | 2.9 | 6.7 | .6 | 5.8 |
| n-$C_9$ | 5.3 | 10.9 | 7.9 | 10.9 |
| Other $C_9$ | 6.2 | 6.4 | 4.7 | 6.3 |
| n-$C_{10}$ | 17.8 | 10.1 | 10.3 | 6.9 |
| Other $C_{10}$ | 5.9 | 6.0 | 6.9 | 6.0 |
| n-$C_{11}$ | 17.5 | 13.6 | 12.5 | 9.9 |
| Other $C_{11}$ | 6.9 | 6.1 | 12.4 | 4.4 |
| Cyclics: | | | | |
| $C_6$ | .2 | | .9 | |
| $C_7$ | 1.2 | 1.3 | 2.1 | 4.4 |
| $C_8$ | 1.6 | 4.1 | 5.2 | 6.9 |
| $C_9$ | 4.9 | 7.2 | 5.7 | 11.6 |
| $C_{10}$ | 6.7 | 8.9 | 12.5 | 9.1 |
| $C_{11}$ | 6.1 | 6.4 | 5.0 | 4.8 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 |

The distribution of the phenols in the tar acids from the cracked and primary naphthas is shown in table 12. Only phenol and 2-methylphenol have boiling points below the nominal cut temperature of the naphthas. Hence, the quantities given in table 12 for most of the compounds represent only part of the material present in the oils from which the

Table 11.—*Aromatic hydrocarbons in primary and cracked shale-oil naphthas, in volume-percent*

| Compound | N–T–U primary naphtha | Recycle-cracked naphtha |
|---|---|---|
| Benzene | 0.3 | 0.8 |
| Toluene | 4.9 | 4.8 |
| Ethylbenzene | 2.0 | 2.9 |
| p-Xylene | 4.2 | 2.2 |
| m-Xylene | 12.8 | 10.7 |
| o-Xylene | 5.6 | 4.2 |
| iso-Propylbenzene | .5 | 1.0 |
| n-Propylbenzene | .7 | 1.1 |
| 1-Methyl-3-ethylbenzene | 1.1 | .5 |
| 1-Methyl-4-ethylbenzene | 11.6 | 11.5 |
| 1,3,5-Trimethylbenzene | 6.8 | 4.0 |
| 1-Methyl-2-ethylbenzene | | |
| tert-Butylbenzene | 12.2 | 11.3 |
| 1,2,4-Trimethylbenzene [1] | | |
| iso-Butylbenzene | | |
| sec-Butylbenzene | | |
| 1-Methyl-2-isopropylbenzene | 19.2 | 29.5 |
| 1-Methyl-3-isopropylbenzene | | |
| 1,2,3-Trimethylbenzene | | |
| 1-Methyl-4-isopropylbenzene [1] | | |
| 1,3-Diethylbenzene | 2.6 | 3.0 |
| 1,4-Diethylbenzene | 15.5 | 12.5 |
| Total | 100.0 | 100.0 |

[1] Most probable compound as indicated by ultraviolet-absorption data.

naphthas were distilled. Therefore, there may not actually be as much difference between the two materials as is indicated by the results in the table. However, it appears that the primary naphtha contains substantially greater relative quantities of the lower boiling homologs, particularly phenol and 4-methylphenol, than does the cracked naphtha.

From the preceding data it appears that primary and cracked shale-oil naphthas will be similar in many respects. From recycle operations, a naphtha may be obtained that differs substantially from the others in hydrocarbon-group analysis. However, even in this case the distribution of compound types within each group is somewhat similar.

TABLE 12.—*Phenols in primary and cracked shale-oil naphthas, in volume-percent*

| Compound | N-T-U primary naphtha | Recycle-cracked naphtha |
|---|---|---|
| Phenol | 14.1 | 5.9 |
| 2-Methylphenol | 23.0 | 16.8 |
| 3-Methylphenol | 13.1 | 9.9 |
| 4-Methylphenol | 22.6 | 7.1 |
| 2-Ethylphenol | 1.8 | 2.6 |
| 3-Ethylphenol | ---------- | .4 |
| 4-Ethylphenol | .9 | ---------- |
| 2,3-Dimethylphenol | 5.2 | 4.1 |
| 2,4-Dimethylphenol | 9.0 | 32.9 |
| 2,5-Dimethylphenol | 3.5 | 10.6 |
| 2,6-Dimethylphenol | 6.7 | 8.1 |
| 3,5-Dimethylphenol | ---------- | 1.6 |
| 2,4,6-Trimethylphenol | .1 | ---------- |

## PROCESSED NAPHTHAS AND GASOLINES

Gasoline boiling-range materials are produced in some foreign countries by commercial methods. Samples of these products, most of which are finished motor fuels, were secured by Bureau of Mines personnel during visits to the countries.[41–44] Data given in table 13 show, in general, that the samples have the compositions that would be expected from discussions in the previous sections. The materials all have a high olefin content—usually in the vicinity of 40 pct. The nitrogen content on the finished gasolines has been reduced essentially to zero. The sulfur is in most cases somewhat less than shown for the raw naphthas in table 8 (no samples were available corresponding to the high-sulfur naphthas from the Marecaux and Cantieny retorts), but it is substantially higher than in the usual petroleum gasoline produced in the United States. In all except two samples from Sweden the sulfur is predominantly residual, presumably thiophenic, as is the case for N-T-U naphtha. The two Swedish gasolines show high contents of thiols and sulfides. Nearly all the samples have tar-acid and tar-base contents below 1 pct.

TABLE 13.—*Analyses of processed naphthas and gasolines*

| Description of sample | Hydrocarbon analysis, vol.-pct. | | | Sulfur, wt.-pct. | Nitrogen, wt.-pct. |
|---|---|---|---|---|---|
| | Saturates | Olefins | Aromatics | | |
| Light gasoline (Sweden) | 47 | 42 | 11 | 1.46 | 0.00 |
| Crude gasoline (Sweden) | 28 | 35 | 37 | 1.45 | .10 |
| Motor gasoline (Sweden) | 50 | 33 | 17 | .25 | .00 |
| Crude gasoline (Pumpherston, France) | 42 | 42 | 16 | .35 | .14 |
| Motor fuel (Pumpherston, France) | 44 | 40 | 16 | .27 | .00 |
| Gasoline (Lantz, France) | 38 | 43 | 19 | .20 | .00 |
| Motor fuel (Scotland) | 50 | 43 | 7 | .10 | .01 |
| Scrubber naphtha (Australia) | 42 | 51 | 7 | .20 | .01 |
| Pressure distillate (Australia) | 43 | 46 | 11 | .23 | .05 |
| Acid-treated heavy naphtha (Australia) | 43 | 40 | 17 | .31 | .00 |
| Caustic-treated light naphtha (Australia) | 44 | 52 | 4 | .11 | .00 |
| Motor fuel (Australia) | 38 | 47 | 15 | .23 | .00 |
| Gasoline (Spain) | 42 | 44 | 14 | .39 | .09 |
| Pressure distillate (South Africa) | 46 | 38 | 16 | .38 | .24 |
| Motor fuel (South Africa) | 49 | 40 | 11 | .36 | .00 |

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[41] Guthrie, Boyd, and Klosky, Simon, The Oil-Shale Industries of Europe: Bureau of Mines Rept. of Investigations 4776, 1951, 73 pp.

[42] Kraemer, A. J., and Thorne, H. M., Oil-Shale Operations in New South Wales, Australia: Bureau of Mines Rept. of Investigations 4796, 1951, 48 pp.

[43] Thorne, H. M., and Kraemer, A. J., Oil Shale in Spain: Bureau of Mines Rept. of Investigations 4736, 1950, 21 pp.

[44] ———, Oil-Shale Operations in the Union of South Africa, October 1947: Bureau of Mines Rept. of Investigations 5019, 1954, 31 pp.

# ANALYSES OF SHALE-OIL NAPHTHAS

Analyses of a number of naphthas are reported in this section. These analyses were performed over a period of several years so that the analytical techniques used, while generally similar for all, were modified periodically to incorporate newly developed improvements. In this section the analyses are reported in approximately the reverse order of their preformance so that the analysis using the best techniques is reported first. A comprehensive analysis, which included an extensive examination of both hydrocarbons and nonhydrocarbons, was performed on a primary naphtha from N–T–U shale oil. Somewhat less elaborate analytical schemes were applied to a Pumpherston naphtha, a Hayes naphtha, a thermally cracked N–T–U naphtha, and two naphthas from oils produced by high-temperature retorting. A brief naphtha analysis that forms a part of the Bureau of Mines Crude Shale Oil Analysis Method [45] was applied to naphthas distilled from a number of American and foreign shale oils. Also, some processed naphthas and gasolines obtained from foreign sources were examined.

## PRIMARY N–T–U NAPHTHA

The primary N–T–U naphtha was obtained from experimental operations of the Bureau of Mines at Rifle, Colo. The naphtha was prepared in refining equipment [46] [47] at Rifle from crude shale oil produced from Green River shale in an N–T–U-type [48] retort. A topping distillation, at atmospheric pressure to a cut temperature of 200° C., yielded 5.6 wt.-pct. (6.5 vol.-pct.) naphtha. Properties of the raw naphtha are shown in table 14.

Tar acids were extracted from the raw naphtha by successive treatments with aqueous 10 pct. sodium hydroxide. The extractions were made at room temperature on 67.7 l. (54.2 kg.) of the naphtha in a 30-gal., glass-lined tank equipped with an external stainless steel pipe and pump circuit. The pump suction drew from the bottom of the tank and the discharge was sprayed horizontally, through small holes drilled radially in the closed end of the introduction pipe, a little below the surface of the liquid in the tank. The first extraction was made with 5 l. of sodium hydroxide for 30 min. After settling to permit phase separation, the aqueous extract was withdrawn and the raffinate was extracted twice more with 5-l. quantities of fresh caustic solution. An analytical check of the raffinate from the third extraction showed no diminution of volume when a portion was shaken with fresh caustic solution. About 10 l. of the caustic-treated naphtha was retained for special studies.

Tar bases were extracted from the remainder of the caustic-treated naphtha by seven successive treatments with 5- to 7-l. quantities of aqueous 10 pct. sulfuric acid. Nitrogen analyses of the raffinates indicated that additional extraction would accomplish no further removal of nitrogen bases. The final raffinate was washed once with 2 pct. caustic solution and twice with distilled water to give a neutral naphtha. Yields obtained from these treatments are given in table 15 on a no-loss basis.

Properties of the neutral naphtha are shown in table 16. The specific gravity is lower than that of the raw naphtha because both the tar acids and the tar bases that were removed have higher gravities than do the hydrocarbons. The neutral naphtha contains most of the sulfur but only about a third of the nitrogen originally present in the naphtha. Although extraction with aqueous acid was repeated until no additional removal of nitrogen was obtained, about half of the nitrogen in the neutral naphtha is basic by nonaqueous titration.

TABLE 14.—*Properties of raw N–T–U naphtha*

| | |
|---|---|
| Specific gravity, 15.6°/15.6° C | 0.8077 |
| Gravity ° API | 43.7 |
| ASTM distillation at 760 mm: | |
| Initial boiling point ° C | 67 |
| 10 percent ° C | 141 |
| 50 percent ° C | 167 |
| 90 percent ° C | 189 |
| End point ° C | 213 |
| Recovery percent | 98.0 |
| Residue do | .4 |
| Loss do | 1.6 |
| Sulfur weight-percent | 1.24 |
| Nitrogen do | 1.21 |
| Basic nitrogen do | 1.00 |

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[45] Stevens, R. F., Dinneen, G. U., and Ball, John S., Analysis of Crude Shale Oil: Bureau of Mines Rept. of Investigations 4898, 1952, 20 pp.

[46] Lankford, J. D., and Morris, Boyd, Refining of Colorado Shale Oil—A Review of Work by the U.S. Bureau of Mines: Oil Shale and Cannel Coal, vol. 2, Inst. Petrol., London, 1951, pp. 500–532.

[47] Lankford, J. D., and Ellis, C. F., Shale Oil Refining: Ind. Eng. Chem., vol. 43, 1951, pp. 27–32.

[48] Cattell, R. A., Guthrie, Boyd, and Schramm, L. W., Retorting Colorado Oil Shale—A Review of the Work of the Bureau of Mines, U.S. Department of the Interior: Oil Shale and Cannel Coal, vol. 2, Inst. Petrol., London, 1951, pp. 345–398.

TABLE 15.—*Yields of products from extraction of N–T–U naphtha*

| | Weight-percent | Volume-percent |
|---|---|---|
| Tar acids | 1. 9 | 1. 5 |
| Tar bases | 6. 6 | 5. 6 |
| Neutral naphtha | 91. 5 | 92. 9 |

TABLE 16.—*Properties of neutral N–T–U naptha*

| | | |
|---|---|---|
| Specific gravity, 15.6°/15.6° C | | 0. 7965 |
| Gravity | ° API | 46. 2 |
| Hydrocarbon-group analysis: | | |
| Paraffins and cycloparaffins | volume-percent | 34 |
| Olefins | do | 45 |
| Aromatics plus sulfur and nitrogen compounds | do | 21 |
| Sulfur | weight-percent | 1. 10 |
| Nitrogen | do | . 39 |
| Basic nitrogen | do | . 22 |

## HYDROCARBONS

Detailed examination of the hydrocarbons was accomplished by a fractional distillation followed by analysis of the fractions using a variety of techniques. Six liters of the neutral naphtha was distilled, at a reflux ratio of 60:1, through a column containing Stedman screen packing. The column was vacuum jacketed, was equipped with an automatic takeoff device, and had the following dimensions: Height, 6 ft.; diameter, 1 in. This column had an efficiency of about 60 theoretical plates at total reflux at atmospheric pressure. In order to obtain a maximum amount of the naphtha overhead, approximately 400 ml. of n-tetradecane was used as a pusher. The naphtha was topped to remove 162 ml. of light ends that could not be fractionated efficiently in the equipment used. After separation of this material, 178 fractions, each containing 28 to 30 ml., were taken. The first 26 pct. of the distillate was obtained at the prevailing barometric pressure of about 585 mm. of mercury. The next 44 pct. was taken at a pressure of 200 mm. and the remainder at 100 mm. The successive reductions in pressure were made to lower the distillation temperatures, thus reducing the tendency for decomposition. Total overhead product was 90 pct. of the charge, with the distillation loss amounting to 3 pct. Distillation data obtained in this manner (corrected to 760 mm.) and densities of the fractions collected are shown in figure 8. Although the sample contains material covering the com-

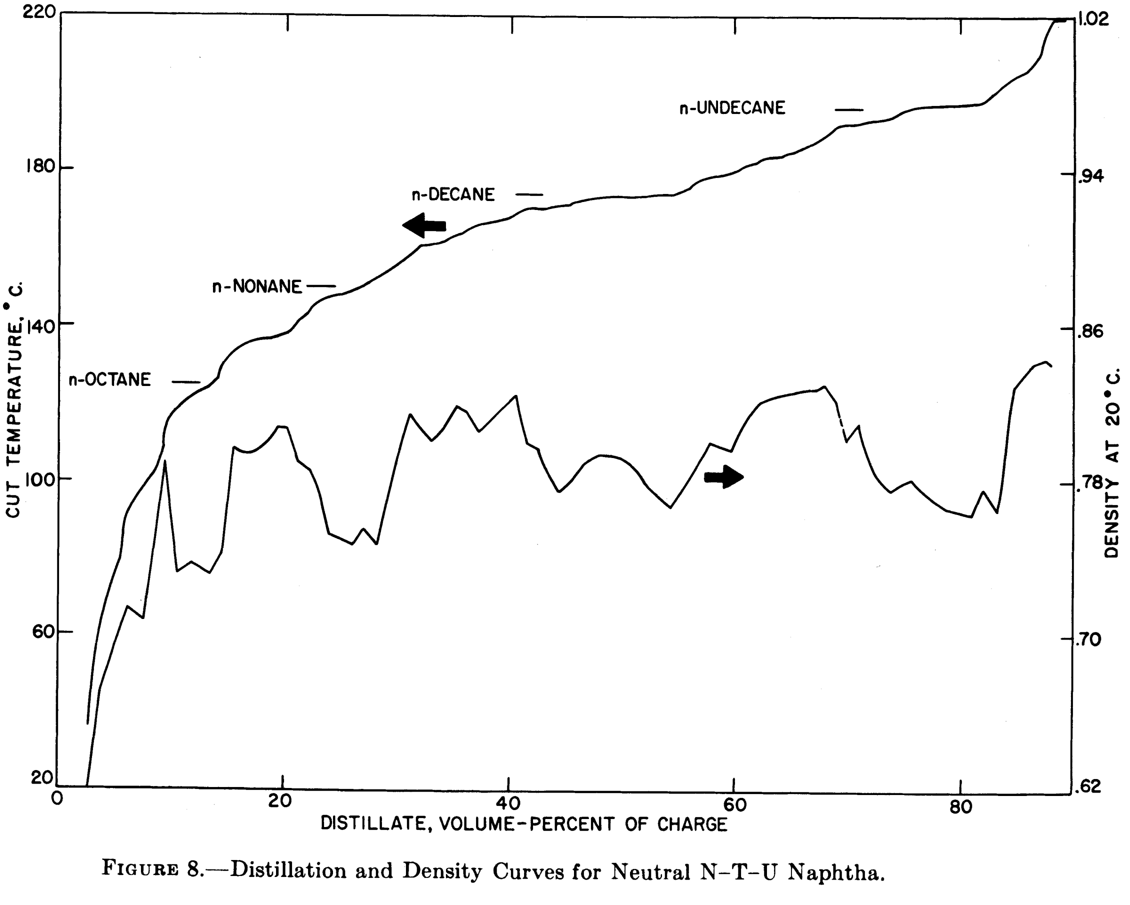

FIGURE 8.—Distillation and Density Curves for Neutral N–T–U Naphtha.

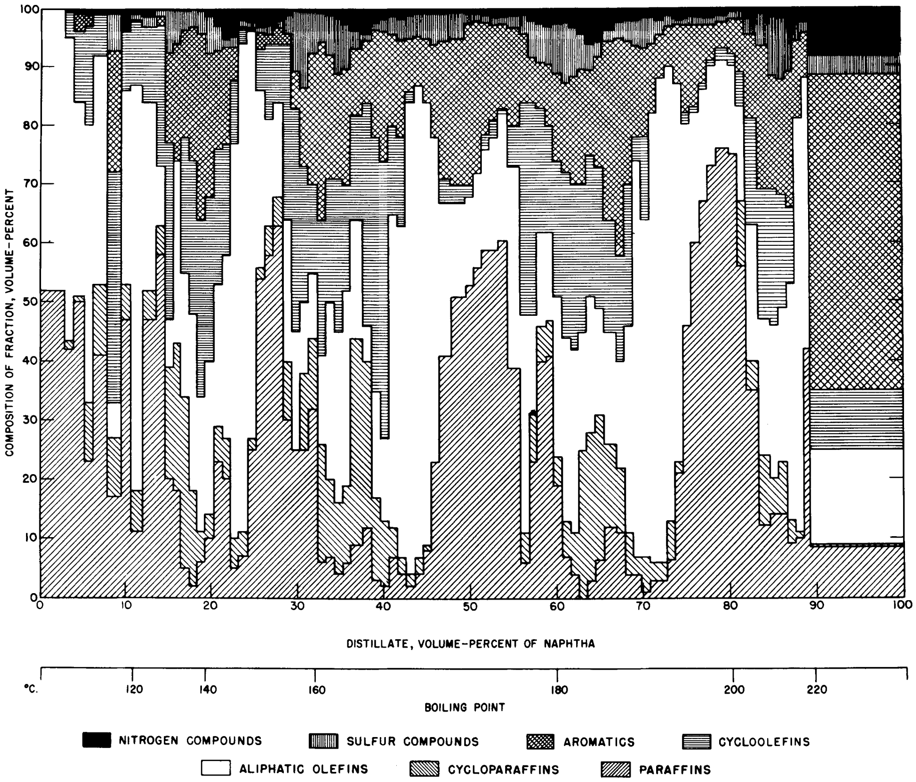

FIGURE 9.—Composition of Fractions From Distillation of Neutral N-T-U Naphtha.

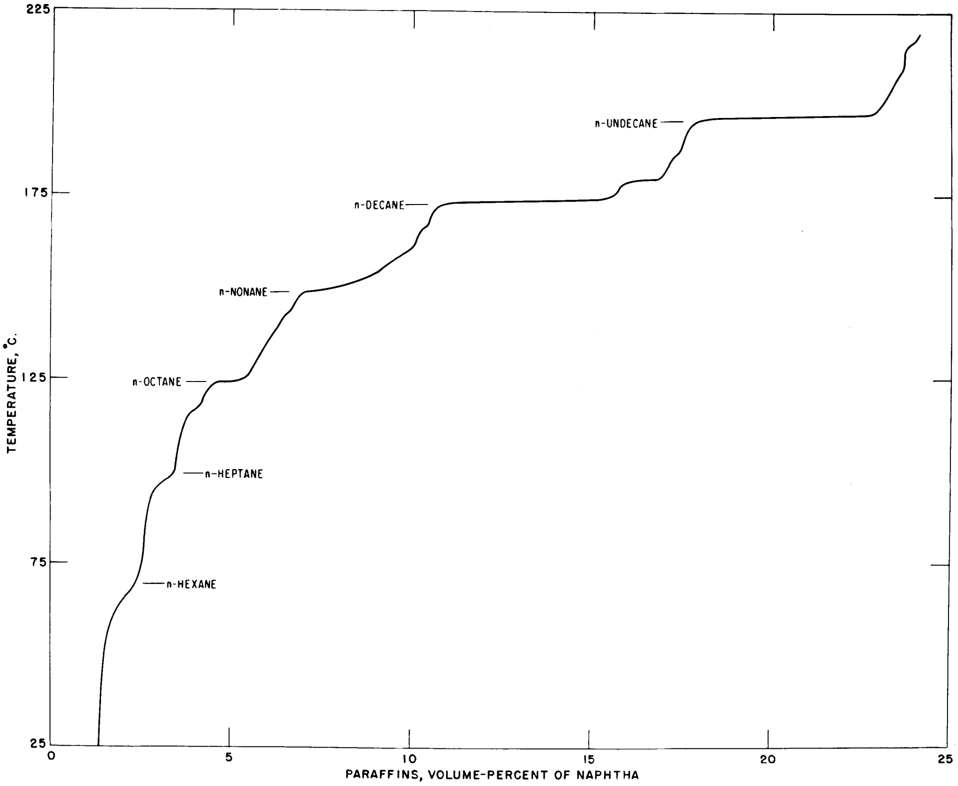

FIGURE 10.—Boiling-Range Distribution of Paraffins in Neutral N-T-U Naphtha.

plete range from room temperature to the cut temperature of the naphtha, a large part of the sample boils in the $C_{10}$ and $C_{11}$ range. Some of the minima in the density curve correspond closely to the plateaus in the distillation curve caused by normal paraffins.

Before analysis, groups of the 178 distillation fractions were combined on the basis of similarities in densities and boiling points to give 83 fractions. Each of these was analyzed by the silica-gel-adsorption method, which is described in the section on analytical methods. Use of this procedure gave a value for the content of paraffins, cycloparaffins, aliphatic olefins, cycloolefins, aromatics, sulfur compounds, and nitrogen compounds. These values, showing the distribution of each type of compound with respect to the volume of naphtha distilled, are shown in figure 9.

The quantities of individual compounds and molecular-weight groups were calculated from the data in figures 8 and 9. To do this, a distribution curve with respect to temperature was plotted for each class of compounds as illustrated for paraffins by figure 10. From the curves obtained, the quantity of each hydrocarbon class distilled per degree rise in temperature was estimated and plotted against temperature. The resulting graphs, figure 11, have peaks (where a large volume of distillate was obtained over a narrow temperature interval) corresponding to large concentrations of a given compound or a group of close-boiling compounds. The quantities of these compounds or groups of compounds were estimated from the areas under the appropriate peaks. Results of such estimates are given in table 17. To aid in identifying the predominant aromatic compound in a fraction, an ultraviolet absorption spectrum was run on each of the fractions. An example of the data obtained is given in figure 12, which shows the ultraviolet spectra for two successive fractions. Fraction 33 has a peak at 2,718 angstroms (A.), which could be due to either 1-methyl-2-ethylbenzene or 1,3,5-trimethylbenzene, as these compounds have very similar boiling points. Fraction 34 shows no peak for these compounds, but has peaks at 2,758 and 2,665 A. that are characteristic of

TABLE 17.—*Hydrocarbons in neutral N-T-U naphtha*

| | Volume-percent |
|---|---|
| Paraffins: | |
| Pentanes | 1.46 |
| n-Hexane | .58 |
| Branched hexanes | .41 |
| n-Heptane | .61 |
| Branched heptanes | .44 |
| n-Octane | 1.44 |
| Branched octanes | .86 |
| n-Nonane | 1.57 |
| Branched nonanes | 1.84 |
| n-Decane | 5.29 |
| Branched decanes | 1.75 |
| n-Undecane | 5.62 |
| Branched undecanes | 2.06 |
| n-Dodecane | .49 |
| Branched dodecanes | .46 |
| Higher boiling compounds | .70 |
| Total | 25.58 |
| Cycloparaffins: | |
| $C_6$ | 0.06 |
| $C_7$ | .36 |
| $C_8$ | .48 |
| $C_9$ | 1.46 |
| $C_{10}$ | 1.98 |
| $C_{11}$ | 1.82 |
| $C_{12}$ | .43 |
| Higher boiling compounds | .04 |
| Total | 6.63 |
| Aliphatic olefins: | |
| Pentenes | 1.34 |
| Hexenes | .74 |
| n-Heptenes | .58 |
| Branched heptenes | .74 |
| n-Octenes | 1.73 |
| Branched octenes | .23 |
| n-Nonenes | 3.03 |
| Branched nonenes | 1.82 |
| n-Decenes | 3.97 |
| Branched decenes | 2.67 |
| n-Undecenes | 4.80 |
| Branched undecenes | 4.77 |
| n-Dodecenes | 1.02 |
| Branched dodecenes | 2.79 |
| Higher boiling compounds | 1.30 |
| Total | 31.53 |
| Cyclic olefins: | |
| $C_6$ | .34 |
| $C_7$ | .79 |
| $C_8$ | 1.99 |
| $C_9$ | 2.18 |
| $C_{10}$ | 4.84 |
| $C_{11}$ | 1.92 |
| $C_{12}$ | 1.19 |
| Higher boiling compounds | .80 |
| Total | 14.05 |
| Aromatics: | |
| Benzene | .07 |
| Toluene | .41 |
| Ethylbenzene | .25 |
| p-Xylene | .19 |
| m-Xylene | .92 |
| o-Xylene | .36 |
| Styrene | .02 |
| Isopropylbenzene | .08 |
| n-Propylbenzene | .09 |
| 1-Methyl-4-ethylbenzene | .99 |
| 1-Methyl-3-ethylbenzene | .04 |
| 1-Methyl-2-ethylbenzene | .34 |
| 1,3,5-Trimethylbenzene | |
| 1,2,4-Trimethylbenzene [1] | .97 |
| iso-Butylbenzene | |
| sec-Butylbenzene | |
| tert-Butylbenzene | |
| 1,2,3-Trimethylbenzene | 2.55 |
| 1-Methyl-4-isopropylbenzene [1] | |
| 1-Methyl-3-isopropylbenzene | |
| 1-Methyl-2-isopropylbenzene | |
| 1,4-Diethylbenzene | 1.08 |
| 1,3-Diethylbenzene | .26 |
| Other $C_{10}$-alkylbenzenes | .84 |
| $C_{11}$-alkylbenzenes | 2.67 |
| Naphthalene | .10 |
| Higher boiling compounds | 4.38 |
| Total | 16.61 |
| Grand total | 94.40 |

[1] Predominant compound in group as indicated by ultraviolet absorption data.

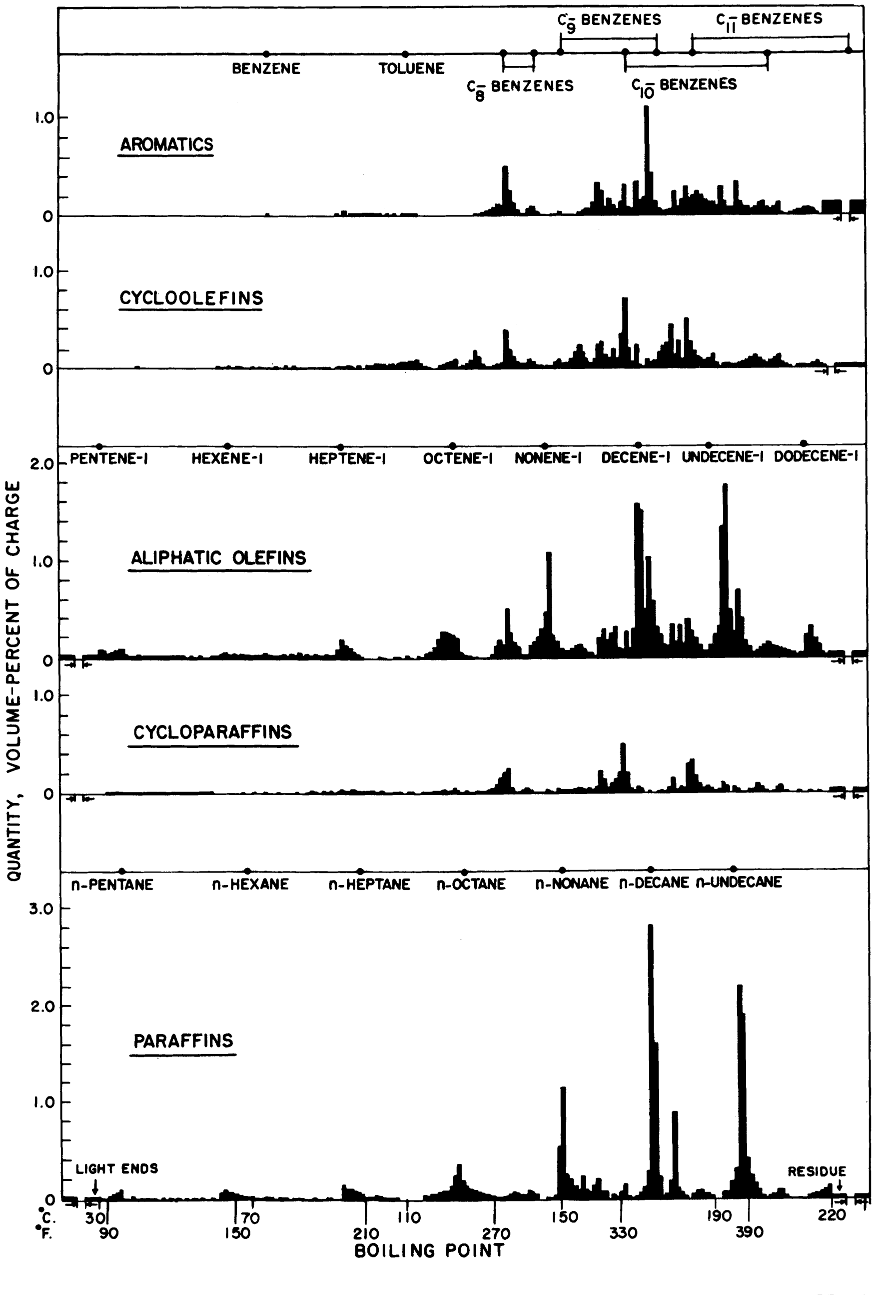

FIGURE 11.—Quantities of Various Classes of Hydrocarbons in Neutral N-T-U Naphtha.

1,2,4-trimethylbenzene. The peak at the lower wave length could be due to tert-butylbenzene, but other peaks characteristic of this compound are absent. Combining the ultraviolet data with adsorption analyses gave the values for aromatics shown in table 17.

The major peaks in the curve for aliphatic olefins in figure 11 generally agree with the boiling points of the straight-chain, terminal olefins. To establish the presence of these compounds, a fraction was selected from each of the peaks. An adsorptogram was run on each fraction, and material in the olefin plateau was collected. Mass and infrared spectra were determined on this material. The mass spectra showed the presence of only aliphatic olefins in the samples. The infrared spectrum corresponded closely to the appropriate terminal olefin and indicated the presence of only small quantities of olefins with internal double bonds. From these results the normal olefins from 1-pentene to 1-undecene were identified.

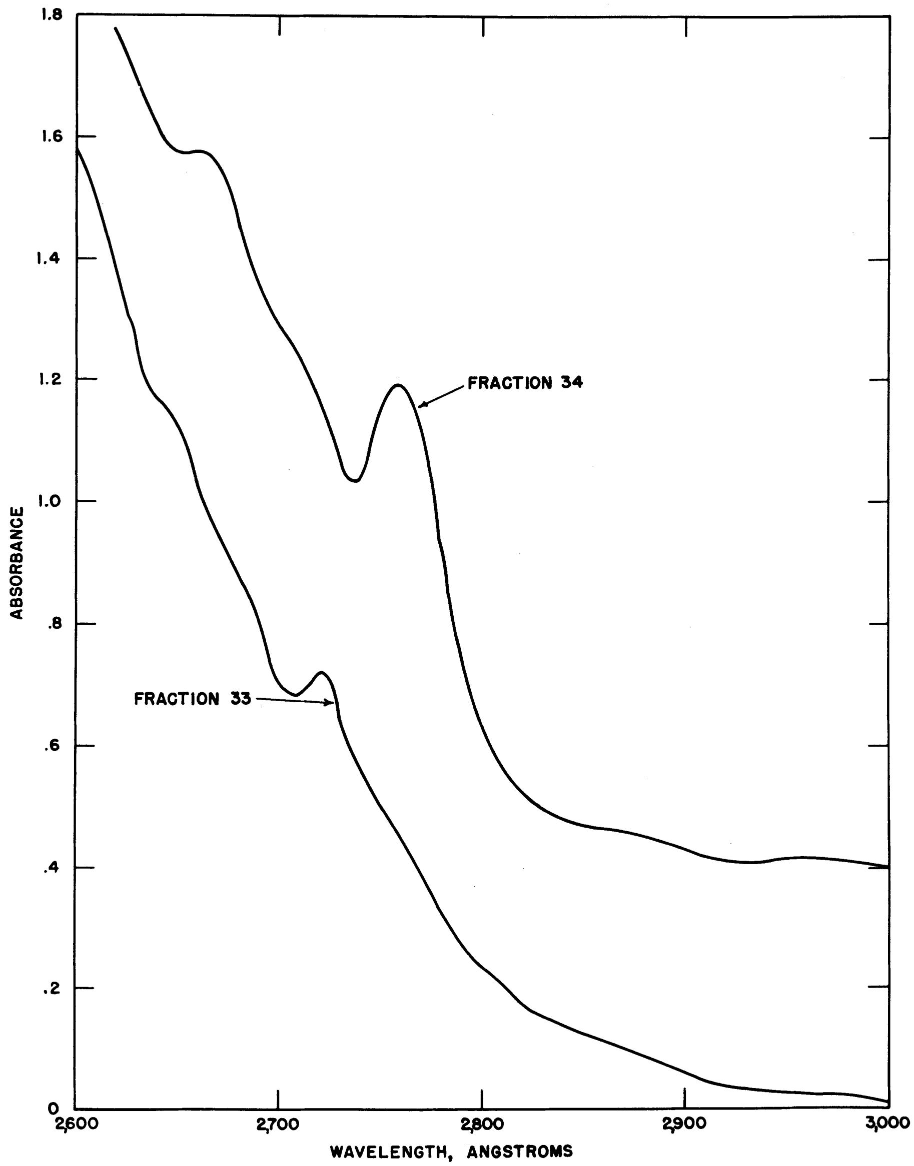

FIGURE 12.—Ultraviolet Spectra of Fractions From Distillation of N-T-U Naphtha.

Because only selected fractions from the distillation were examined, the quantities of terminal olefins present could not be estimated.

## SULFUR COMPOUNDS

The raw naphtha contained 1.24 wt.-pct. sulfur (table 14), and the neutral naphtha contained 1.10 pct. (table 16). Conversion of the latter value to quantity of sulfur-containing compounds in the neutral naphtha indicated the presence of about 4 pct. of such compounds. Their distribution in the neutral naphtha with respect to boiling point was calculated from data obtained during work described in the preceding section. The results are shown in figure 13, in which the definite peaks suggest the predominance of a relatively few compounds. Since thiophenes are thought to be the principal type of sulfur compound present, boiling ranges of molecular-weight groups of thiophenes are given in figure 13 for reference. They are designated according to the total number of carbon atoms in the molecule.

The results of group sulfur analyses[49] on the raw and neutral naphthas are shown in table 18. The values in the table are reported only to a whole number because the reagents for the various types of compounds do not give clean re-

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[49] Ball, John S., Determination of Types of Sulfur Compounds in Petroleum Distillates: Bureau of Mines Rept. of Investigations 3591, 1941, 60 pp.

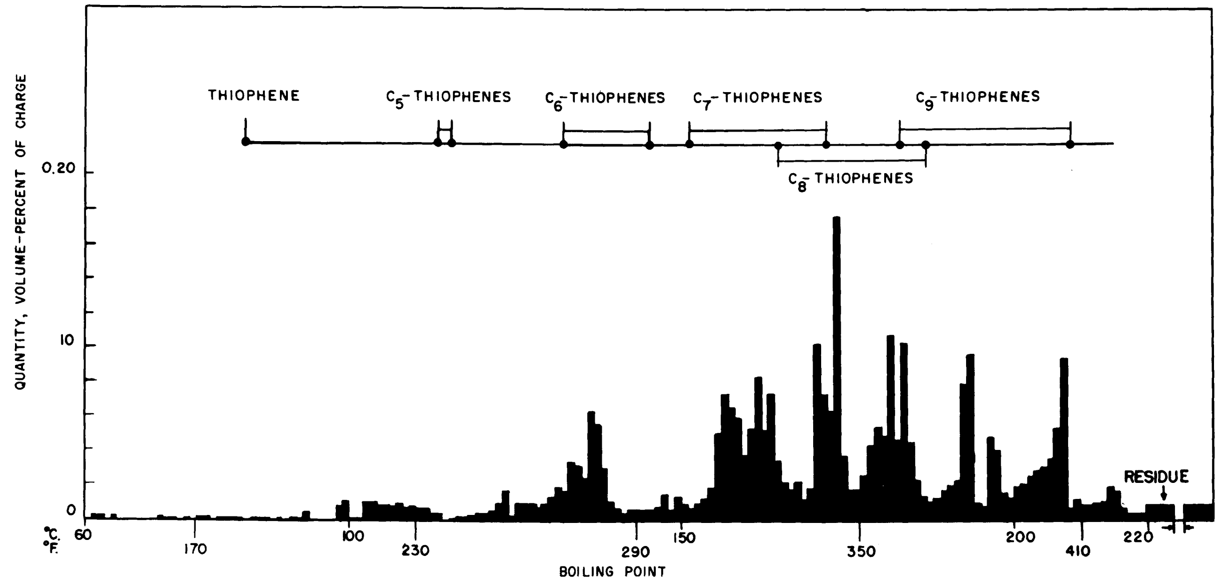

FIGURE 13.—Amounts of Sulfur Compounds in Neutral N-T-U Naphtha.

TABLE 18.—*Group sulfur analyses of N-T-U naphthas*

| Sulfur type | Sulfur present as indicated type, wt.-pct. | |
|---|---|---|
| | Raw naphtha | Neutral naphtha |
| Free sulfur | 0 | 0 |
| Thiol | 4 | 1 |
| Disulfide | 2 | 1 |
| Sulfide | 19 | 18 |
| Residual (including thiophenes) | 75 | 80 |

actions when used on shale-oil distillates. Removal of the aromatic sulfides and thiophenes by extraction with mercuric nitrate could not be applied to the shale-oil naphtha because of the violent reaction of this reagent with the olefins in the naphtha. Consequently, these types of compounds are included in the residual classification along with other nonextractable compounds. The residual sulfur comprises 75 to 80 pct. of the total sulfur, so the investigation of sulfur compounds was directed primarily toward the identification of thiophenes, which were thought to make up the largest part of this classification.

As the first step in the thiophene investigation, about 6 l. of the neutral naphtha was distilled in the same column used for the hydrocarbon work. The distillation was conducted at 580 mm. pressure to a vapor temperature of 138° C. The pressure was reduced to 200 mm. and the distillation continued to a vapor temperature of 142° C. The pressure was then reduced to 100 mm. for the remainder of the distillation. These pressure reductions kept the pot temperature below 175° C., reducing the possibility of thermal decomposition. Approximately one-half-percent cuts (30 ml.) were obtained at a reflux ratio of about 75:1. These cuts were combined on the basis of boiling point and sulfur content to give the fractions shown in table 19. In most instances this technique provided several fractions within each molecular-weight group. It was hoped that some separation among the isomers of a given molecular weight was thus achieved. Thiophenes were separated from each of the composite fractions by a combination of chromatography and derivative formation. The separated thiophenes were identified from spectral and chemical data obtained on them. A detailed description of the concentration and identifica-

TABLE 19.—*Composite fractions prepared for thiophene investigation*

| Fraction | Molecular-weight group, assuming alkyl thiophenes | Boiling range | Sulfur, wt.-pct. |
|---|---|---|---|
| 1 | 84 | 55°- 92° C. | 0.20 |
| 2 | 98 | 92°-118° C. | 1.36 |
| 3 | 112 | 118°-134° C. | 1.22 |
| 4 | 112 | 134°-135° C. | 1.04 |
| 5 | 112 | 135°-139° C. | 2.08 |
| 6 | 112 | 139°-145° C. | .66 |
| 7 | 126 | 145°-152° C. | .44 |
| 8 | 126 | 152°-159° C. | 2.78 |
| 9 | 126 | 159°-161° C. | 1.69 |
| 10 | 126 | 161°-167° C. | 2.05 |
| 11 | 140 | 167°-172° C. | .94 |
| 12 | 140 | 172°-175° C. | .89 |
| 13 | 140 | 175°-180° C. | 1.33 |
| 14 | 140 | 180°-187° C. | 1.52 |
| 15 | 154 | 187°-194° C. | .86 |
| 16 | 154 | 194°-200° C. | .37 |
| 17 | 154 | 200°-205° C. | 1.16 |
| 18 | [1] 154 | 205°-210° C. | 2.30 |

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[1] This fraction also could contain benzothiophene, which has a molecular weight of 134.

tion techniques is given in the section on analytical methods.

## QUALITATIVE IDENTIFICATION OF THIOPHENES

### FRACTION 1 (55°–92° C.)

The concentration procedure yielded a single compound from this fraction. The compound was identified as thiophene by direct comparison of its mass spectrum with that of an authentic sample of thiophene. The close agreement of representative peaks from the two spectra is shown in the following chart:

| Ion | Relative ion intensities | |
|---|---|---|
| | Thiophene from fraction 1 (boiling range 55°–92°C.) | Thiophene (boiling point 84°C.) |
| 86+ | 4. 5 | 4. 4 |
| 84+ | 100. 0 | 100. 0 |
| 83+ | 6. 6 | 6. 1 |
| 69+ | 8. 0 | 7. 1 |
| 58+ | 65. 4 | 65. 4 |

### FRACTION 2 (92°–118° C.)

Only the two isomeric methylthiophenes would be expected in this fraction. The following chart gives selected mass-spectral peaks of the thiophenes from this fraction and of the methylthiophenes:

| Ion | Relative ion intensities | | |
|---|---|---|---|
| | Thiophenes from fraction 2 (92°–118° C.) | 2-Methylthiophene (b.p. 113° C.) | 3-Methylthiophene (b.p. 114° C.) |
| 98+ | 54. 5 | 54. 9 | 53. 3 |
| 97+ | 100. 0 | 100. 0 | 100. 0 |
| 59+ | 4. 1 | 4. 6 | 1. 3 |
| 58+ | 5. 7 | 6. 0 | 4. 5 |

The intensities of the peaks for the material from the fraction fall between those of the known compounds but are much closer to those for 2-methylthiophene. Thus the presence of both of the methylthiophenes is indicated, with 2-methylthiophene predominating.

### FRACTION 3 (118°–134° C.)

A comparison of the spectrum of the thiophenes from this fraction with spectra of thiophenes that would be expected in a fraction of this boiling range follows. For ease of comparison, each of the spectra is calculated with the base or reference peak at the same ion (97+).

| Ion | Relative ion intensities | | | |
|---|---|---|---|---|
| | Thiophenes from fraction 3 (118°–134° C.) | 2-Ethylthiophene (b.p. 132° C.) | 3-Ethylthiophene (b.p. 135° C.) | 2,5-Dimethylthiophene (b.p. 136° C.) |
| 112+ | 91. 2 | 38. 5 | 38. 9 | 135. 5 |
| 111+ | 98. 9 | 7. 4 | 7. 5 | 173. 9 |
| 97+ | 100. 0 | 100. 0 | 100. 0 | 100. 0 |
| 85+ | 3. 1 | 2. 1 | 2. 6 | 3. 8 |
| 84+ | 1. 9 | 2. 1 | 4. 0 | 1. 4 |
| 59+ | 23. 4 | 1. 4 | 1. 4 | 37. 4 |

The high values of the 112+, 111+, and 59+ peaks show that the isolated thiophenes contain a large amount of 2,5-dimethylthiophene mixed with one or both of the ethylthiophenes. The spectra of the ethylthiophenes are similar, with the greatest difference occurring in the values for the 84+ peak. The value for this peak in the spectrum of the isolated thiophenes suggests the presence of 2-ethylthiophene, with the possibility that some 3-ethylthiophene is present.

In order to establish the presence of 3-ethylthiophene and confirm the presence of 2-ethylthiophene, the mercuric chloride derivatives of the thiophenes were prepared. The soluble monoderivative of mercuric chloride with 2-ethylthiophene was removed by leaching from the insoluble di-derivatives of the other two compounds. Thiophenes regenerated from the insoluble derivatives gave the following mass spectrum:

| *Ion* | *Relative ion intensities, thiophenes regenerated from insoluble mercuric chloride derivatives* |
|---|---|
| 112+ | 103. 4 |
| 111+ | 120. 1 |
| 97+ | 100. 0 |
| 85+ | 3. 5 |
| 84+ | 2. 4 |
| 59+ | 28. 5 |

For comparison with the previous results the spectrum is given with the 97+ peak as 100, although this peak is no longer the highest. The increase in relative concentration of the 2,5-dimethylthiophene, resulting from the removal of 2-ethylthiophene, is shown by the higher values of the 112+, 111+, and 59+ peaks. If the thiophenes in the fraction had consisted only of 2-ethylthiophene and 2,5-dimethylthiophene, the increased concentration of 2,5-dimethylthiophene would have caused a decrease in the value of the 84+ peak, so the observed increase of this peak indicates the presence of 3-ethylthiophene.

### FRACTION 4 (134°–135° C.)

Thiophenes from this fraction also contained 2,5-dimethylthiophene as shown by a high 59+ peak in their mass spectrum. Confirmation of the presence of 2,5-dimethylthiophene was made using derivatives. A purified mercuric acetate derivative prepared from the fraction decomposed at 295° to 300° C. compared with 295° to 300° C. for the corresponding derivative of 2,5-dimethylthiophene.

### FRACTION 5 (135°–139° C.)

A comparison of the spectrum of the thiophenes from this fraction with the spectra of the three isomers considered probable from boiling-point data follows:

| Ion | Relative ion intensities | | | |
|---|---|---|---|---|
| | Thiophenes from fraction 5 (135°–139° C.) | 2,5-Dimethylthiophene (b.p. 136° C.) | 2,4-Dimethylthiophene (b.p. 137° C.) | 2,3-Dimethylthiophene (b.p. 140° C.) |
| 112+ | 89.4 | 77.9 | 72.8 | 100.2 |
| 111+ | 100.0 | 100.0 | 100.0 | 100.0 |
| 97+ | 92.6 | 57.5 | 48.5 | 120.2 |
| 85+ | 4.6 | 2.2 | 2.0 | 5.5 |
| 59+ | 14.9 | 21.5 | 7.0 | 16.6 |

The relatively high values of the 112+, 97+, and 85+ peaks show that 2,3-dimethylthiophene is the predominant compound mixed with one or both of the other two compounds. The presence of 2,5-dimethylthiophene cannot be proven from the spectrum, but since it was shown to be in each of the two preceding fractions, it would be expected also in this one. A mixture of 2,5-dimethylthiophene and 2,3-dimethylthiophene would give a value between 16.6 and 21.5 for the 59+ peak; thus the value of 14.9 obtained for the isolated thiophenes is strong indication of the presence of 2,4-dimethylthiophene.

### FRACTION 6 (139°–145° C.)

The spectrum of the thiophene concentrate from this fraction is compared to the spectra of the two highest boiling dimethylthiophenes:

| Ion | Relative ion intensities | | |
|---|---|---|---|
| | Thiophenes from fraction 6 (139°–145° C.) | 2,3-Dimethylthiophene (b.p. 140° C.) | 3,4-Dimethylthiophene (b.p. 145° C.) |
| 112+ | 80.2 | 100.2 | 69.9 |
| 111+ | 100.0 | 100.0 | 100.0 |
| 97+ | 65.6 | 120.2 | 48.8 |
| 59+ | 8.3 | 16.6 | 3.2 |
| 58+ | 7.7 | 13.1 | 2.9 |

From this comparison it is seen that the isolated thiophenes have values intermediate between 2,3- and 3,4-dimethylthiophene. Both of these thiophenes appear to be present.

Additional evidence of the presence of 3,4-dimethylthiophene was obtained by preparing mercuric chloride derivatives and extracting the soluble monoderivative formed by the 2,3-dimethylthiophene from the insoluble di-derivative formed by the 3,4-dimethylthiophene. Following regeneration of the thiophene from the insoluble di-derivative of mercuric chloride, the di-derivative of mercuric acetate was prepared. The acetate derivative melted and decomposed at 261° to 264° C. as compared with 262° to 264° C. for the derivative of 3,4-dimethylthiophene.

### FRACTION 7 (145°–152° C.)

Application of the concentration procedure to this fraction yielded a product that was identified as consisting mainly of 2-isopropylthiophene. The identification was based on the close agreement of the mass spectrum of the isolated material with that of 2-isopropylthiophene, as follows:

| Ion | Relative ion intensities | | |
|---|---|---|---|
| | Thiophenes from fraction 7 (145°–152° C.) | 2-Isopropylthiophene (b.p. 153° C.) | 3-Isopropylthiophene (b.p. 157° C.) |
| 126+ | 27.9 | 27.7 | 34.4 |
| 125+ | 1.7 | 1.9 | 1.7 |
| 111+ | 100.0 | 100.0 | 100.0 |
| 85+ | 6.4 | 6.0 | 6.6 |
| 59+ | 2.5 | 2.2 | 2.1 |

### FRACTION 8 (152°–159° C.)

2-Methyl-5-ethylthiophene was identified as the predominant isomer in the thiophenes isolated from this fraction. The identification was based on a combination of data from mass spectra, formation of mercuric acetate derivatives, and hydrogenation.

By applying the correlations described in the section on analytical methods to the following mass spectrum, all types of substitution other than methylethyl were eliminated, and the methyl group was located in the 2-position:

| *Ion* | *Relative ion intensities, thiophenes from fraction 8* (152°–159° C.) |
|---|---|
| 126+ | 39.9 |
| 125+ | 5.4 |
| 111+ | 100.0 |
| 97+ | 10.0 |
| 59+ | 8.7 |

The higher values for all the peaks as compared with the spectra of the isopropylthiophenes given previously indicate that the principal unknown thiophene is not an isopropylthiophene. It is not one of the n-propylthiophenes, as these compounds lose mass 29 to give the largest or base peak at 97+. It is not a trimethylthiophene because these compounds have the parent (126+) and parent-less-mass-1 (125+) peaks greater than 50 pct. of the base peak. The predominant compound must, therefore, be a methylethylthiophene, as this is the only other possible configuration having the correct molecular weight. As the 59+ peak is between 5 and 15 pct. of the base peak, a methyl group should be in the 2-position.

The location of the ethyl group was determined by the use of mercuric acetate derivatives. The di-derivative formed at both 25° and 60° C., indicating either a 2,5- or a 3,4-disubstituted thiophene. The methyl group having already been located in the 2-position, the compound was identified as 2-methyl-5-ethylthiophene.

The principal alkane resulting from hydrogenation (*see* the section on analytical methods) was identified from its mass spectrum as n-heptane. This supports the identification of 2-methyl-5-ethylthiophene, which gives n-heptane on hydrogenation.

### FRACTION 9 (159°–161° C.)

The thiophene concentrate from this fraction consisted of a complex mixture. No compounds were identified from it.

### FRACTION 10 (161°–167° C.)

A thiophene isolated from this fraction was identified as 2,3,5-trimethylthiophene. Selected peaks from the mass spectrum of the isolated material are shown as follows:

| *Ion* | *Relative ion intensities, thiophenes from fraction 10* (161°–167° C.) |
|---|---|
| 126+ | 77.9 |
| 125+ | 79.1 |
| 111+ | 100.0 |
| 97+ | 4.2 |
| 85+ | 3.1 |
| 59+ | 29.9 |

The parent (126+) and parent-less-mass-1 (125+) peaks are greater than 50 pct. of the base peak, indicating methyl substitution exclusively. The 59+ peak is above 15 pct. of the base peak, showing that methyl groups are in both the 2- and 5-positions. The remaining methyl group must be in the 3-position, so the compound was identified as 2,3,5-trimethylthiophene.

Additional evidence of trisubstitution was obtained by the preparation of mercuric acetate derivatives. The monoderivative formed with mercuric acetate at both 25° and 60° C., which is characteristic only of trisubstituted thiophenes. To provide data for final confirmation of the identification, a sample of 2,3,5-trimethylthiophene was synthesized. A comparison showing the close agreement between the mass spectra of the isolated and synthesized 2,3,5-trimethylthiophenes follows:

| Ion | Relative ion intensities | |
|---|---|---|
| | Isolated 2,3,5-trimethylthiophene | Synthesized 2,3,5-trimethylthiophene |
| 126+ | 77.9 | 79.5 |
| 125+ | 79.1 | 81.5 |
| 111+ | 100.0 | 100.0 |
| 97+ | 4.2 | 5.5 |
| 85+ | 3.1 | 2.9 |
| 59+ | 29.9 | 29.1 |

### FRACTION 11 (167°–172° C.)

This fraction was a transition fraction containing thiophenes having molecular weights of 126 and 140. Mass-spectral data indicated that the predominant compounds were probably 2,3,5-trimethylthiophene and 2-methyl-5-isopropylthiophene. The former compound had been identified in the previous fraction, and positive identification of the latter compound was obtained in the next fraction.

### FRACTION 12 (172°–175° C.)

A thiophene isolated from this fraction was identified as 2-methyl-5-isopropylthiophene. Mass spectral peaks used in establishing the structure of the isolated thiophene are:

| *Ion* | *Relative ion intensities, thiophenes from fraction 12* (172°–175° C.) |
|---|---|
| 140+ | 28.5 |
| 139+ | 2.2 |
| 125+ | 100.0 |
| 111+ | 2.3 |
| 97+ | 9.0 |
| 85+ | 2.4 |
| 59+ | 10.5 |

The 59+ peak is in the 5 to 15 pct. range, so a methyl group is in the 2-position. This indicates that as the unknown has a molecular weight of 140, it must be either a methylpropylthiophene or a dimethylethylthiophene. The base peak at 125+ shows that the isolated thiophene does not contain a n-propyl group, which would lose a mass of 29 to form the base peak at 111+. Preparation of mercuric acetate derivatives yielded the diderivative at both 25° and 60° C. As only 2,5- and 3,4-disubstituted thiophenes react in this way, and as a methyl group is in the 2-position, the compound was identified as 2-methyl-5-isopropylthiophene.

Confirmation of the proposed structure was obtained from data on a sample of synthesized 2-methyl-5-isopropylthiophene. The similarity of the mass spectra of the isolated and synthesized compounds is shown by the following results:

| Ion | Relative ion intensities | |
|---|---|---|
| | Isolated 2-methyl-5-isopropylthiophene | Synthesized 2-methyl-5-isopropylthiophene |
| 140+ | 28.5 | 28.3 |
| 139+ | 2.2 | 1.7 |
| 125+ | 100.0 | 100.0 |
| 111+ | 2.3 | .3 |
| 97+ | 9.0 | 8.3 |
| 85+ | 2.4 | 2.2 |
| 59+ | 10.5 | 10.8 |

A comparison of the 111+ peaks shows an impurity in the isolated compound, probably a sec-butylthiophene.

### FRACTION 13 (175°–180° C.)

Identification of the preponderant thiophene isomer isolated from this fraction was made from mass spectral correlations and hydrogenation. The spectrum showed the presence of a thiophene of molecular weight 140. The base peak was at 111+, showing the loss of an ethyl group, which occurs in this molecular-weight group only from a sec-butylthiophene or a methyl-n-propylthiophene. The 59+ peak in the spectrum was 10.0 pct. of the base peak, showing the presence of a methyl group in the 2-position. Hydrogenation of the isolated thiophenes yielded a mixture of octanes, the preponderant one being n-octane. 2-Methyl-5-n-propylthiophene is the only compound that satisfies all of the data; thus, it was identified as the predominant isomer in the fraction.

### FRACTION 14 (180°–187° C.)

Mass-spectral correlations applied to the thiophenes isolated from this fraction indicated that a thiophene of molecular weight 140 was losing a methyl group to form the base peak at 125+. Mercuric acetate derivatives showed trisubstitution, as only the monoderivative formed at 25° and 60° C. The only possible trisubstituted thiophenes having a molecular weight of 140 are dimethylethylthiophenes. Hydrogenation of the isolated thiophenes yielded primarily a mixture of 3-methylheptane and 4-methylheptane. The only trisubstituted thiophenes which would form these two octanes on hydrogenation are 2,3-dimethyl-5-ethylthiophene and 2,4-dimethyl-5-ethylthiophene, respectively. The isolated thiophenes were thus indicated to be a mixture of these two compounds.

### FRACTION 15 (187°–194° C.)

Mass-spectral correlations showed that the thiophene concentrate isolated from this fraction contained a thiophene of molecular weight 154 that lost an ethyl group to form the base peak at 125+. A methyl group was in the 2-position, as the 59+ peak was between 5 and 15 pct. of the base peak. The only isomers with spectra fulfilling both these requirements are the methyl-sec-butylthiophenes and the dimethyl-n-propylthiophenes. Diderivatives formed with mercuric acetate at both 25° and 60° C., indicating either 2,5- or 3,4-substitution. Thus, the compound was identified as 2-methyl-5-sec-butylthiophene.

### FRACTIONS 16–18 (194°–210° C.)

On the basis of sulfur contents, three composite fractions were prepared from the material in this boiling range. However, the only individual compound isolated from them was benzo[b]thiophene, which was predominantly in the fraction boiling between 205° and 210° C. The identification was made by comparing the ultraviolet and mass spectra of the isolated material with those of an authentic sample of benzo[b]thiophene. The ultraviolet absorption curves are shown in figure 14, and selected peaks in the mass spectra of the two compounds are compared as follows:

| Ion | Relative ion intensities | |
|---|---|---|
| | Isolated benzo[b] thiophene | Known benzo[b] thiophene |
| 135+ | 9.1 | 8.0 |
| 134+ | 100.0 | 100.0 |
| 108+ | 5.5 | 3.7 |
| 90+ | 8.9 | 8.1 |
| 67+ | 9.9 | 9.2 |

## QUANTITATIVE ESTIMATION OF THIOPHENES

In addition to qualitative identifications, an estimate of abundance is necessary in order to evaluate the importance of each compound. As mass spectra were available for all the thiophenes having a molecular weight of 112 or less, the isolated materials in this range could be analyzed quantitatively. The results of such analyses on the aromatic-thiophene concentrates from the first six composite fractions are given in table 20. The results shown differ in some instances from those reported previously [50] owing to some revisions in the calculations. However, the changes do not alter conclusions that are drawn from the results.

Reference spectra were available for only a few of the thiophenes having molecular weights of 126 and above, so that complete quantitative analyses could not be made. However, the composite fractions from the distillation were prepared on the basis of peaks in the sulfur concentration, and it was found in most instances

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[50] Kinney, I. W., Jr., Smith, J. R., and Ball, J. S.; Thiophenes in Shale-Oil Naphtha: Anal. Chem., vol. 24, 1952, pp. 1749–1754.

TABLE 20.—*Quantity of thiophenes having molecular weights or 112 of less in N–T–U naphtha*

| Compound | Molecular weight | Proportion of total sulfur in neutral naphtha represented by compound, wt.-pct. | Compounds in neutral naphtha, vol.-pct. |
|---|---|---|---|
| Thiophene | 84 | 0.35 | 0.01 |
| 2-Methylthiophene | 98 | 3.70 | .10 |
| 3-Methylthiophene | 98 | .49 | .01 |
| 2-Ethylthiophene | 112 | 1.21 | .04 |
| 3-Ethylthiophene | 112 | .30 | .01 |
| 2,5-Dimethylthiophene | 112 | 4.14 | .13 |
| 2,4-Dimethylthiophene | 112 | .71 | .02 |
| 2,3-Dimethylthiophene | 112 | 1.67 | .05 |
| 3,4-Dimethylthiophene | 112 | .31 | .01 |

that a peak contained a single isomer in predominant quantities. Hence, an estimate as to relative abundance was made from sulfur content and distillation data. The results of such estimations are given in table 21. The values are somewhat high, as the minor constituents in each fraction were not considered.

## IDENTIFICATION OF CYCLIC SULFIDES

The group sulfur analysis, table 18, shows that, except for the residual classification, the sulfur in the naphtha consisted largely of sulfides with much smaller amounts of thiols and disulfides. Some small-scale preliminary experiments were made to determine the best method of isolating the sulfides. Concentrates of sulfur compounds and aromatic hydrocarbons were prepared from both raw and neutral naphthas by adsorption on silica gel or alumina or by successive use of the two. The concentrates were treated with mercurous nitrate to extract the sulfides, and the solid product was reacted with potassium iodide to regenerate the sulfides. Examination of the recovered oils showed that they were too complex to permit any identifications to be made. Qualitative tests[51] indicated the presence of thiophenes, aliphatic sulfides, and cyclic sulfides. It was, therefore, decided to prepare a sufficient amount of concentrate by adsorption to permit a fractional distillation before attempting identifications.

TABLE 21.—*Approximate quantity of thiophenes having molecular weights of 126 or above in N–T–U naphtha*

| Compound | Molecular weight | Proportion of total sulfur in neutral naphtha represented by compound, wt.-pct. | Compounds in neutral naphtha, vol.-pct. |
|---|---|---|---|
| 2-Isopropylthiophene | 126 | 1 | 0.05 |
| 2-Methyl-5-ethylthiophene | 126 | 9 | .3 |
| 2,3,5-Trimethylthiophene | 126 | 6 | .2 |
| 2-Methyl-5-n-propylthiophene | 140 | 6 | .2 |
| 2-Methyl-5-isopropylthiophene | 140 | 7 | .25 |
| 2,4-Dimethyl-5-ethylthiophene | 140 | 8 | .3 |
| 2,3-Dimethyl-5-ethylthiophene | 140 | | |
| 2-Methyl-5-sec-butylthiophene | 154 | 4 | .2 |
| Benzo[b]thiophene | 134 | 2 | .1 |

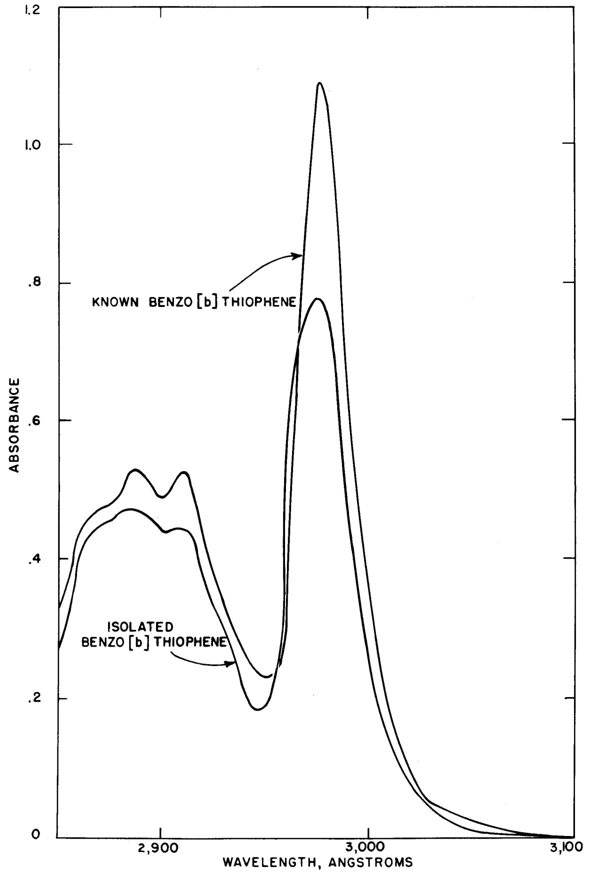

FIGURE 14.—Ultraviolet Spectra of Benzo[b]thiophene.

### PREPARATION OF SULFIDE CONCENTRATE

About 16 l. of neutral naphtha was passed in 4-l. batches through silica gel using a 1:1 weight ratio of adsorbent to naphtha. A displacement technique using acetone was employed. The percolate was collected until 75 pct. by volume of the charge had issued from the column. At this point, the receiver was changed and the remainder of the charge was collected. These second fractions from the four runs were combined, and the acetone was removed by distillation. Approximately 4 l. of the concentrate of aromatic hydrocarbons and sulfur compounds, having a sulfur content of 4.66 wt.-pct., was obtained. About 85 pct. of the sulfur originally present in the naphtha was recovered in this concentrate. The combined first fractions contained about 10 pct. of the sulfur

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[51] Karr, Clarence, Jr., Evaluation of Twenty Qualitative Tests for Petroleum Sulfur Compounds: Anal. Chem., vol. 26, 1954, pp. 528-536.

originally present, but this sulfur was nearly all thiophenic and therefore was ignored in this part of the work.

The concentrate prepared by the previous operation was processed further, using activated H–41 alumina (Alcoa) at an adsorbent-to-sample ratio of 12:1. Four fractions were obtained by eluting successively with n-pentane, 10 pct. benzene in pentane, benzene, and acetone. Most of the desired sulfur compounds, those reactive toward mercurous nitrate, were in the benzene-eluted fraction. The bulk of the benzene was stripped from the fraction, and the residual material was vapor-transferred to separate volatile materials from polymers. The distillate contained 5.37 wt.-pct. sulfur, most of which was reactive toward mercurous nitrate. The sulfur in this fraction represented about 85 pct. of the nonthiophenic sulfur originally present in the naphtha.

### IDENTIFICATION OF COMPOUND TYPE

A 50-ml. sample of the sulfide concentrate was charged to a semimicro distillation column, and fractions containing about 1 ml. each were taken. Several fractions of sulfur-free material, largely benzene, were obtained at the beginning of the distillation, and these were followed by fractions having sulfur contents between 10 and 19 pct. The fractions were in the boiling range from 143° to 194° C. at 760 mm. pressure. Mass spectra of the fractions showed the presence of many types of compounds but indicated the predominance of a homologous series having molecular weights of 88, 102, 116, 130, 144, and 158. These weights correspond to cyclic or unsaturated sulfides, but the spectra were too complex to permit identifications.

An attempt was made to separate cyclic sulfides from other materials by formation of mercuric chloride complexes using the procedure described by Emmot.[52] However, only dark gummy materials rather than crystalline complexes were formed. Apparently the other substances present in the fractions interfered with the desired reaction.

The preceding results showed the necessity for further purification of the sulfide concentrate before identification work. A portion of the benzene-eluted fraction that had not been distilled was eluted from alumina with pentane. The sulfur was largely concentrated in the first three fractions obtained. These were combined and passed through silica gel using a displacement technique with 2-propanol as the desorbent. The first 50 pct. of the charge that emerged from the column was relatively low in sulfur. The last 50 pct. to emerge had a sulfur content of about 20 wt.-pct. This material was distilled and mass spectra obtained on the fractions. The homologous series having molecular weights from 88 through 158 was again evident, and compounds from more than one molecular-weight group were present in each fraction. However, the additional separation steps had removed enough of the impurities so that interpretation of the spectra indicated that the homologous series consisted principally of cyclic sulfides.

### IDENTIFICATION OF INDIVIDUAL COMPOUNDS

After the presence of cyclic sulfides as a class had been established, an attempt was made to isolate and identify several of the lower-molecular-weight homologs. Fractions from the distillation of the neutral naphtha described under the section on hydrocarbon compounds were used. These fractions were utilized because of availability and because they represented essentially an expanded distillation for the sulfides. A few of the fractions in the boiling range of a given cyclic sulfide were selected. These fractions did not correspond to the peaks in sulfur concentration shown in figure 13, as these are due largely to thiophenes. The selected fractions were combined and percolated through silica gel using an adsorbent-to-sample ratio of 7:1. The course of the percolation was followed by the refractive index and volume sum of material issuing from the column. The last fractions from the column contained most of the sulfides. These fractions were recombined and percolated through 50 g. of silica gel. Fractions of about 1 ml. each were taken and tested for reactive sulfur with alcoholic mercuric chloride. All fractions giving a positive test were combined and treated with alcoholic mercuric chloride. The precipitate was washed several times with hot absolute ethanol. The solution was refrigerated, and supernatant liquid was decanted between washings. The purified precipitate was dried and then steam-distilled with aqueous potassium iodide. The resultant oil-water distillate was extracted with pentane, and the pentane was removed by distillation. Mass and infrared spectra were determined on the recovered oil.

The mass spectrum of a sample prepared by the above method showed that it consisted chiefly of material having a molecular weight of 102. A comparison of selected peaks from the spectrum of the unknown with those of the three cyclic sulfides having a molecular weight of 102 is shown in table 22. The spectrum of the unknown corresponds closely to that of 2-methylthiacyclopentane but differs markedly from the spectra of the other two compounds.

The mass spectrum of another sample showed that it was predominantly material

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[52] Emmot, R., Investigations of the Sulfur Compounds Present in Middle Distillate-$SO_2$ Extracts: Jour. Inst. Petrol., vol. 39, 1953, pp. 695–714.

TABLE 22.—*Mass-spectral data used to establish the identity of an unknown as 2-methylthiacyclopentane*

| Ion | Relative ion intensities | | | |
|---|---|---|---|---|
| | Unknown | 2-Methylthiacyclopentane | 3-Methylthiacyclopentane | Thiacyclohexane |
| 102+ | 42.5 | 42.4 | 87.9 | 100.0 |
| 88+ | 5 | 5.0 | 2.4 | 5.3 |
| 87+ | 100 | 100.0 | 44.8 | 98.1 |
| 74+ | 15 | 16.3 | 50.2 | 22.1 |
| 69+ | 3 | 3.5 | 24.1 | 19.0 |
| 67+ | 6 | 5.4 | 8.9 | 41.0 |
| 61+ | 7 | 7.5 | 15.3 | 63.3 |
| 60+ | 20 | 19.2 | 100.0 | 45.0 |
| 59+ | 21 | 20.4 | 30.7 | 25.2 |
| 45+ | 36 | 32.5 | 56.1 | 68.2 |

having a molecular weight of 116. This would indicate that it consisted of one or more of the dimethylthiacyclopentanes, ethylthiacyclopentanes, or methylthiacyclohexanes. The spectrum of the unkown material is compared in table 23 with the spectra of the few of these compounds that were available for reference. The data show that the unknown is not on of the methylthiacyclohexanes or a combination of them. The spectrum of the unknown corresponds fairly closely to that of 2,5-dimethylthiacyclopentane, indicating that the unknown probably consisted primarily of this compound with smaller quantities of other isomers. The lack of other reference spectra, however, prevented a positive identification.

The mass spectrum of another of the extracted oils showed the presence of compounds having molecular weights of 116 and 130. Examination of the available reference compounds showed that for thiacyclohexane homologs, summation of the peaks at m/e of 45, 59, 61, 67, 69, 74, 115, and 116 gave a substantially higher value than summation of the peaks at m/e of 60, 87, 88, 101, and 102. For thiacyclopentanes, the reverse was true. In the sample under consideration, the summation of the former set of peaks was about 300, whereas that of the latter set was about 200. This suggested that the sample consisted primarily of thiacyclohexanes. An infrared spectrum on the sample indicated the presence of an ethyl group and suggested 3-and/or 4-substitution. These data suggested that the peak at 116 was due to the presence of methylthiaclohexanes with the methyl group on 3- or 4-position. They also indicated that ethylthiacyclohexanes with the ethyl group on the 3- or 4-position contributed to the 130 peak. However, the data neither supported nor denied the presence of dimethylthiacyclohexanes in the compounds of molecular weight 130.

TABLE 23.—*Mass-spectral data used to establish the identity of an unknown as a dimethylthiacyclopentane*

| Ion | Relative ion intensities | | | | |
|---|---|---|---|---|---|
| | Unknown | 2,5-Dimethylthiacyclopentane | 2-Methylthiacyclohexane | 3-Methylthiacyclohexane | 4-Methylthiacyclohexane |
| 116+ | 47 | 38 | 51 | 75 | 103 |
| 101+ | 100 | 100 | 100 | 100 | 100 |
| 87+ | 4 | 2 | 32 | 14 | 12 |
| 74+ | 33 | 30 | 8 | 13 | 15 |
| 67+ | 32 | 24 | 37 | 46 | 83 |
| 61+ | 23 | 24 | 21 | 42 | 70 |
| 60+ | 25 | 20 | 32 | 38 | 51 |
| 59+ | 39 | 40 | 28 | 19 | 27 |

## NITROGEN COMPOUNDS

Naphthas from Colorado shale oils generally contain about 1 pct. nitrogen, which is equivalent to about 10 pct. nitrogen-containing compounds. As shown in table 14, a little over 80 pct. of this nitrogen can be titrated as basic material. Most of the basic nitrogen compounds were extracted by aqueous acid. However, some of the basic compounds, as well as practically all of the nonbasic nitrogen compounds, remained in the neutral oil. Consequently, identification of nitrogen compounds involved work on the tar bases extracted both from the raw naphtha and from the residual neutral naphtha.

### IDENTIFICATION OF PYRIDINES

Attempts to isolate and identify individual pyridines were confined to material removed from the naphtha by extraction with aqueous acid. The aqueous solution was washed several times with pentane to remove residual neutral oil and then made strongly alkaline with aqueous 20 pct. sodium hydroxide to liberate the organic bases. The organic layer was separated from the mother liquor, which was extracted with diethyl ether to recover dissolved bases. After removal of the ether, the residue was combined with the main portion of the separated tar bases. The recovered tar bases amounted to 5.6 vol.-pct. (table 15) of the naphtha. A sample of the bases was fractionally distilled through the Stedman column described previously in the discussion on hydrocarbons. The results are shown by the distillation curve in figure 15, which has several distinct plateaus. Fraction number was used as the abscissa because the subsequent discussion of the identification of individual compounds, most of which are shown in figure 15, will refer to the fractions in which they were found. The fractions were not all of the same size, so the relative lengths of the plateaus are not significant.

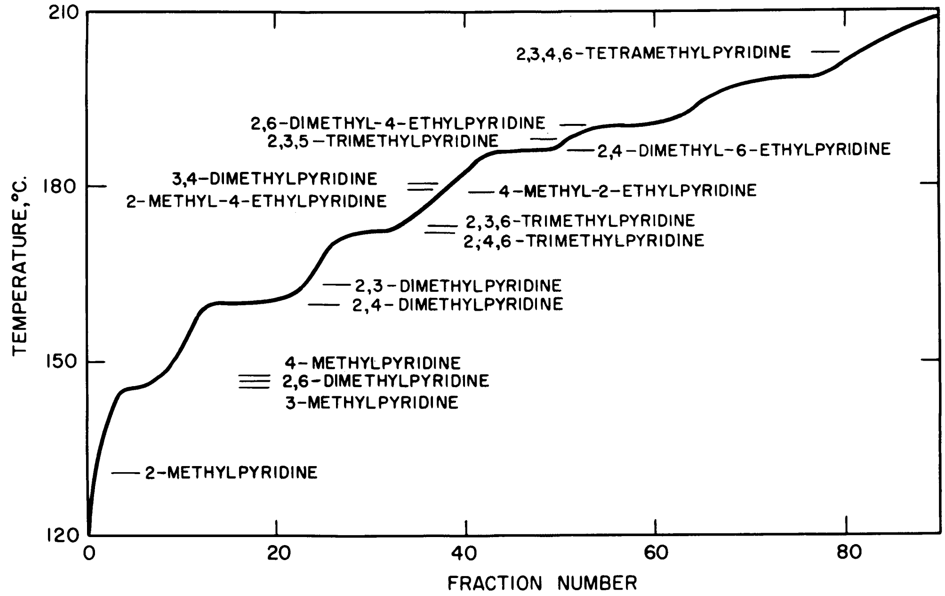

Figure 15.—Distillation of Tar Bases From Primary N-T-U Naphtha.

Individual pyridine homologs were identified from spectral and chemical data on fractions selected from distillation plateaus and transition zones. Although a given fraction usually contained more than one compound, an infrared spectrum of the fraction frequently had a sufficient number of characteristic peaks to identify an individual compound. Such identifications are illustrated in table 24 for one of the fractions in which a compound occurred. The commonly used chemical-identification method was the melting point of the

Table 24.—*Identification of pyridines by infrared spectroscopy*

| | Absorption peaks used for identification, wavelength in microns [1] |
|---|---|
| Pyridine | 10.10, 9.70, 9.37 |
| Fraction 1 | 10.10, 9.69, 9.36 |
| 2-Methylpyridine | 14.13, 13.70, 13.30, 12.50, 10.25, 10.02, 9.52, 9.07 |
| Fraction 1 | 14.18, 13.68, 13.30, 12.51, 10.25, 10.02, 9.53, 9.07 |
| 3-Methylpyridine | 9.72, 9.57, 9.05, 8.87 |
| Fraction 5 | 9.70, 9.58, 9.04, 8.86 |
| 4-Methylpyridine | 14.02, 12.50, 10.30, 9.62, 9.34 |
| Fraction 9 | 14.02, 12.52, 10.28, 9.60, 9.33 |
| 2,6-Dimethylpyridine | 13.70, 12.90, 9.13, 8.64 |
| Fraction 6 | 13.71, 12.87, 9.11, 8.62 |
| 2,4-Dimethylpyridine | 13.75, 13.25, 12.73, 12.20, 10.96, 10.30, 10.05, 9.65 |
| Fraction 19 | 13.72, 13.23, 12.71, 12.23, 10.93, 10.27, 10.05, 9.68 |
| 2,3-Dimethylpyridine | 11.70, 10.91, 9.78, 9.32, 8.88, 8.45 |
| Fraction 25 | 11.70, 10.93, 9.79, 9.35, 8.90, 8.47 |
| 2,4,6-Trimethylpyridine | 13.72, 11.85, 10.82, 10.07 |
| Fraction 32 | 13.75, 11.88, 10.83, 10.06 |
| 2,3,6-Trimethylpyridine | 12.28, 9.99, 9.82, 8.86 |
| Fraction 35 | 12.29, 10.01, 9.82, 8.85 |
| 2-Methyl-4-ethylpyridine | 13.38, 11.98, 11.23, 10.04, 9.61, 8.57 |
| Fraction 40 | 13.37, 11.98, 11.21, 10.03, 9.65, 8.57 |
| 2,4-Dimethyl-6-ethylpyridine | 12.25, 11.82, 11.13, 10.62, 10.32, 9.39 |
| Fraction 42 | 12.29, 11.84, 11.14, 10.61, 10.32, 9.41 |
| 2,6-Dimethyl-4-ethylpyridine | 11.67, 11.24, 10.03, 9.69, 9.39, 8.17 |
| Fraction 59 | 11.65, 11.25, 10.03, 9.72, 9.40, 8.18 |
| 2,3,4,6-Tetramethylpyridine | 13.54, 11.68, 11.20, 10.47, 9.91, 8.64, 8.16 |
| Fraction 81 | 13.51, 11.66, 11.18, 10.45, 9.90, 8.62, 8.15 |

[1] Only clearly defined peaks were used in the identifications. Peaks that were obscured by other components, or that were not definite because of low concentration of the identified compound, are not shown. In each case the number of unique peaks was sufficient for positive identification.

TABLE 25.—*Identification of pyridines by chemical techniques*

| Compound | Boiling point of compound, ° C. [1] | Found principally in fractions boiling at ° C. (760 mm.) | Picrate obtained from fraction No. | Melting point of picrate, ° C. | | |
|---|---|---|---|---|---|---|
| | | | | Literature [1] | Found | Mixed |
| Pyridine | 115.3 | Up to 131 | | 165-166 | | |
| 2-Methylpyridine | 128-129 | Up to 145 | 1-2 | 165.5 | 165-167.5 | 166-167.5 |
| 3-Methylpyridine | 144.6 | 145-149 | | 149-150 | | |
| 4-Methylpyridine | 145.3 | 145-149 | | 167 | | |
| 2,6-Dimethylpyridine | 144.4 | 145-149 | 6 | 163 | 163-164.5 | 164-165 |
| 2,4-Dimethylpyridine | 158 | 160 | 19 | 182.5-183 | 182.5-183.5 | 183-184 |
| 2,3-Dimethylpyridine | 162-164 | 164 | 25 | 187-188 | 185-188 | 188-189 |
| 2,4,6-Trimethylpyridine | 170.3 | 170-173 | 26 | 155.5-156 | 155-156.5 | 156.5-158 |
| 2,3,6-Trimethylpyridine | 173-174 | 174 | 35-36 | 146-148 | 147.5-148.5 | 147-148.5 |
| 4-Methyl-2-ethylpyridine | 178.7 | 175-180 | 36-38 | 115-116 | 122-124 | 121.5-122.5 |
| | [2] 177-179 | | | [2] 120-121 | | |
| | | | | [3] 122-123 | | |
| 2-Methyl-4-ethylpyridine | 177-179 | 182 | 40 | 141-142 | 144-145 | 143.5-144.5 |
| 3,4-Dimethylpyridine | 163.5-164.5 | 182 | 40 | 163 | 161.5-163 | |
| | [4] 179 | | | | | |
| 2,4-Dimethyl-6-ethylpyridine | [5] 164.2-166.4 | 184-185 | 45 | [5] 113.3-114.3 | 113.9-114.9 | 112.9-114.1 |
| 2,3,5-Trimethylpyridine | [4] 186.8 | 187 | 56 | [4] 184 | 182-184 | 183.5-184 |
| 2,6-Dimethyl-4-ethylpyridine | [6] 184-186 | 189-192 | 60 | [6] 121 | 120.9-121.1 | 120.4-121.4 |
| 2,3,4,6-Tetramethylpyridine | [4] 203.3 | 210 | 81 | [4] 107 | 106-107 | 106.5-107.5 |

[1] Except as noted values in these columns obtained from Morton, A. A., Chemistry of Heterocyclic Compounds: McGraw-Hill Book Co., New York, N.Y., 1946, p. 206.

[2] Chichibabin, A. E., 4-Methyl-2-ethylpyridine: Jour. Russ. Phys. Chem. Soc., vol. 54, 1924, pp. 607-610.

[3] Hackman, J. T., Wibaut, J. P., and Gitsel, H. P. L., Basic Nitrogen Compounds From Cracked Distillates of California Petroleum: Rec. trav. chim., vol. 62, 1943, pp. 229-253.

[4] Eguchi, T., Basic Nitrogen Compounds From Fushun Shale Tar II: Bull. Chem. Soc., Japan, vol. 3, 1928, pp. 227-243.

[5] This paper. Boiling point determined at a pressure of 575 mm. Hg.

[6] Siddiqui, R. H., Pyridine Series I. Attempt to Synthesize 2-Methyl-4-ethylpyridine: Jour. Indian Chem. Soc., vol. 16, 1939, pp. 410-414.

picrate. Such data and the particular fractions on which they were obtained are shown in table 25.

### PYRIDINE

The presence of a small amount of pyridine in fraction 1 was established by comparing selected peaks in the infrared spectrum of the fraction with those of reference material as shown in table 24.

### 2-METHYLPYRIDINE

This compound was present in fractions 1 to 4. Selected infrared spectral data on fraction 1 are shown in table 24, and the melting point of picrates obtained from fractions 1 and 2 is shown in table 25.

### 3-METHYLPYRIDINE, 4-METHYLPYRIDINE, AND 2,6-DIMETHYLPYRIDINE

These three compounds have similar boiling points (table 25) and are the major components in the fractions 5 to 9 which make up the first plateau in the distillation curve (fig. 15). As would be expected from their boiling points, infrared spectra of the fractions indicate that those at the front of the plateau contain a greater concentration of 3-methylpyridine, whereas those at the rear of the plateau contain a greater concentration of 4-methylpyridine. The presence of 2,6-dimethylpyridine was substantiated by the melting point of a picrate from fraction 6 (table 25).

### 2,4-DIMETHYLPYRIDINE

Infrared data showed this compound to be present in fractions 10 through 24 (fraction 19 is given in table 24) and indicated that it was the major constituent in the plateau at about 160° C. on the distillation curve. Confirmation of the identity of the compound was obtained from the melting point (table 25) and X-ray diffraction pattern of the picrate. The diffraction pattern of the unknown picrate is compared in figure 16 with the patterns of two of the compounds that might be expected in the fractions on the basis of boiling-point data. The patterns for the unknown and for 2,4-dimethylpyridine appear to be identical.

### 2,3-DIMETHYLPYRIDINE

The presence of 2,3-dimethylpyridine in one of the transition fractions between the second and third plateaus on the distillation curve was

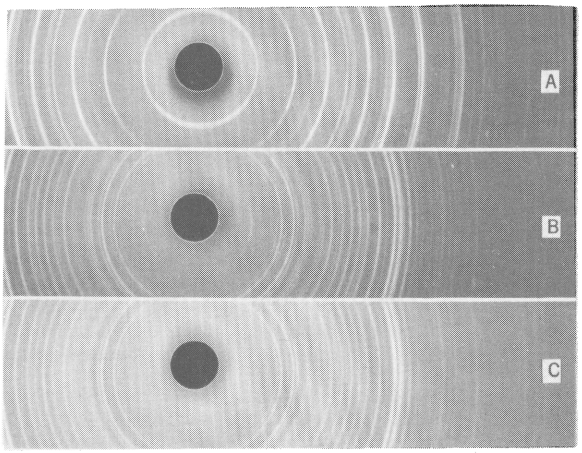

FIGURE 16.—Identification of Unknown Dimethylpyridine Picrate From X-Ray Diffraction Patterns. Note: (A) 2,3-Dimethylpyridine picrate, (B) Unknown picrate, (C) 2,4-Dimethylpyridine picrate.

TABLE 26.—*Identification of 2,4,6-trimethylpyridine*

| Fraction | Melting point of picrate, ° C. | | |
|---|---|---|---|
| | Literature | Found | Mixed |
| 26 | 155. 5–156 | 155–156. 5 | 156. 5–158 |
| 32 | | 155. 5–157. 5 | 157–158. 5 |
| 33 | | 155–158 | 156–158 |
| 34 | | 153–157 | 155. 5–158 |
| 35 | | 156–158 | 156. 5–158. 5 |

indicated by infrared data (table 24). Melting point (table 25) and X-ray diffraction pattern of a picrate from the fraction confirmed the presence of this compound.

### 2,4,6-TRIMETHYLPYRIDINE

The fractions in the third plateau on the distillation curve contained primarily 2,4,6-trimethylpyridine. This is shown by the data in table 26, which gives the melting points of picrates obtained from several fractions in the plateau. The infrared spectra of fractions 26 to 35 also showed the presence of 2,4,6-trimethylpyridine as illustrated by that for fraction 32, given in table 24.

### 2,3,6-TRIMETHYLPYRIDINE

In addition to the picrate of 2,4,6-trimethylpyridine, fraction 35 yielded a picrate with a melting point of 147.5° to 148.5° C. A picrate of this same melting point was also obtained from fraction 36. A mass spectrum of basic material regenerated from the picrate showed the presence of a compound having a molecular weight of 121. Comparison of selected peaks in the spectrum of the unknown with those of 2,3,6-trimethylpyridine, as given in table 27, shows close agreement, indicating that the unknown was 2,3,6-trimethylpyridine. An infrared spectrum of fraction 35 (table 24) and mixed melting point of the picrates (table 25) substantiated the identification of the unknown compound as 2,3,6-trimethylpyridine.

TABLE 27.—*Mass spectra of compound from fraction 36 and of 2,3,6-trimethylpyridine*

| Ion | Relative ion intensities | |
|---|---|---|
| | Material from fraction 36 | 2,3,6-trimethylpyridine |
| 121+ | 100. 0 | 100. 0 |
| 120+ | 58. 0 | 59. 4 |
| 106+ | 19. 5 | 16. 4 |
| 53+ | 10. 3 | 12. 7 |
| 52+ | 11. 1 | 10. 9 |
| 51+ | 16. 5 | 17. 2 |
| 42+ | 16. 9 | 12. 9 |
| 39+ | 22. 9 | 21. 5 |

### 4-METHYL-2-ETHYLPYRIDINE

Fraction 36 contained, in addition to 2,3,6-trimethylpyridine, a compound that yielded a picrate of melting point 122° to 124° C. Picrates of the same melting point from fractions 37 and 38 indicated the presence of the same compound in these fractions, A mass spectrum of the regenerated compound showed it to have a molecular weight of 121 and a relatively large peak (about 60 pct. of the largest peak in the spectrum) at the molecular weight minus 15, indicating the probable presence of an ethyl group. A picrolonate from fraction 37 melted at 175° to 176° C., which is close to the value of 172° to 173° C. given in the literature [53] for the picrolonate of 4-methyl-2-ethylpyridine. As no reference material was available for comparison with the unknown compound, a sample of 4-methyl-2-ethylpyridine was synthesized. This was accomplished by heating 40 g. of 4-methylpyridine and 70 g. of ethyl iodide in a closed tube at 315° C. for 14 hr. The product was dissolved in acid, and neutral oil was removed. It was then causticized and steam-distilled to recover the nitrogen bases. The bases were fractionally distilled through a small packed column. A picrate was prepared from the fraction boiling from 172° to 176° C. The mixed melting point (table 25) of the picrate from this fraction with the picrate of the unknown confirmed the identification of 4-methyl-2-ethylpyridine.

### 2-METHYL-4-ETHYLPYRIDINE

A picrate from fraction 40 had a melting point of 144° to 145° C. The mass spectrum of the regenerated compound showed a molecular weight of 121 and a peak with an intensity of 65 pct. at the molecular weight minus 15, indicating the probable presence of an ethyl group. A reference sample of 2-methyl-4-ethylpyridine was synthesized by reacting 2-methylpyridine, acetic anhydride, zinc, and acetic acid.[54] The product was fractionally distilled and the picrate prepared from material in a plateau boiling at 178° to 179° C. A mixed melting point of the picrates (table 25) indicated that the unknown and synthesized compounds were identical. Also, the infrared spectrum of the fraction 40 indicated the presence of 2-methyl-4-ethylpyridine.

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[53] Hackman, J. T., Wibaut J. P., and Gitsel, H. P. L., Basic Nitrogen Compounds From Cracked Distillates of California Petroleum: Rec. trav. chim., vol. 62, 1943, pp. 229–253.

[54] Shriner, R. L., Organic Syntheses: John Wiley and Sons, Inc., New York, N.Y. vol. 27, 1947, pp. 38–39.

### 3,4-DIMETHYLPYRIDINE

Fraction 40 yielded an additional picrate which melted at 161.5° to 163° C. A mass spectrum of material regenerated from the picrate showed a molecular weight of 107. As the unknown was found in a fraction containing a methylethyl homolog, the compound was probably one of the two highest boiling dimethyl homologs, 3,4-dimethylpyridine or 3,5-dimethylpyridine. The mass spectrum of the unknown is compared in table 28 with the spectra of these two compounds. The unknown corresponds somewhat more closely to the spectrum of 3,4-dimethylpyridine than it does to that of 3,5-dimethylpyridine. Also, the melting points of several derivatives of the unknown agreed well with those given in the literature for 3,4-dimethylpyridine derivatives, whereas the 3,5-dimethylpyridine derivatives have quite different values. The picrate melting point agrees with the literature value for 3,4-dimethylpyridine (table 25). The hexachloroplatinate melted at 267° to 269° C., compared with a literature value [55] of 276° C. The picrolonate melted at 221° to 224° C., compared with the 223° to 228° C. given in the literature.[56] It therefore appears that 3,4-dimethylpyridine was present in fraction 40.

TABLE 28.—*Mass spectra of compound from fraction 40 and of reference compounds*

| Ion | Relative ion intensities | | |
|---|---|---|---|
| | Material from fraction 40 | 3,4-Dimethylpyridine | 3,5-Dimethylpyridine |
| 107+ | 100.0 | 100.0 | 100.0 |
| 106+ | 52.6 | 48.5 | 48.7 |
| 92+ | 21.8 | 21.5 | 21.2 |
| 79+ | 38.5 | 38.1 | 35.7 |
| 78+ | 7.8 | 7.3 | 7.7 |
| 77+ | 15.0 | 14.2 | 15.1 |
| 66+ | 5.5 | 5.6 | 7.2 |
| 65+ | 10.6 | 11.3 | 8.3 |
| 53+ | 11.4 | 11.5 | 10.1 |
| 52+ | 14.3 | 13.1 | 10.7 |
| 51+ | 20.5 | 18.0 | 15.4 |
| 50+ | 12.9 | 10.8 | 8.9 |
| 39+ | 35.4 | 33.8 | 37.0 |

### 2,4-DIMETHYL-6-ETHYLPYRIDINE

In the fractions above number 40, picrate derivatives did not form readily. This difficulty appeared to be due to interference by pyrroles, which were shown to be present by positive reaction of the fractions to Ehrlich's reagent.[57] A number of techniques, including adsorption, refluxing with strong acid or base, air oxidation, acetylation, and treatment with nitrous acid, chromic acid, or benzene diazonium chloride, were investigated for the removal of pyrroles. The benzene diazonium chloride reaction gave the greatest yield of product having a negative Ehrlich test. This technique was, therefore, applied to fraction 41 and all subsequent fractions studied.

Fractions 41 through 51 formed the fourth plateau on the distillation curve. Fractions 41, 42, 45, 48, and 51 gave picrates melting at 113° to 116° C., so it appeared that the compound giving this picrate was the principal component in the plateau. A mass spectrum of material regenerated from the picrate showed a molecular weight of 135 but did not yield any information as to types of substituent groups. Ultraviolet and infrared spectra indicated the probability of 2,4,6-trisubstitution. Considering this and the prevalence of 2,4,6-trimethylpyridine in the naphtha, it was thought that there was a good possibility that the compound under investigation was either 2,6-dimethyl-4-ethylpyridine or 2,4-dimethyl-6-ethylpyridine. Hence, these two compounds were synthesized.

Synthesis of the 2,6-dimethyl-4-ethylpyridine was accomplished by reacting ethyl acetoacetate, propional, and ammonia in alcoholic solution to give diethyl 2,6-dimethyl-4-ethyl-1,4-dihydropyridine-3,5-dicarboxylate.[58] An ether solution of this product was oxidized by nitrous oxide to give diethyl 2,6-dimethyl-4-ethylpyridine-3,5-dicarboxylate,[59] which was hydrolyzed with alcoholic potassium hydroxide and distilled from soda lime to yield 2,6-dimethyl-4-ethylpyridine.

The other isomer, 2,4-dimethyl-6-ethylpyridine, was prepared by heating a mixture of 2,4-dimethylpyridine and ethyl iodide in a sealed tube at 300° C. The product was fractionally distilled to obtain the 2,4-dimethyl-6-ethylpyridine.

Comparison of the properties of the unknown compound with those of the synthesized compounds showed it to be 2,4-dimethyl-6-ethylpyridine. Mass-spectral data (table 29)

TABLE 29.—*Mass spectra of compound from fractions 41 to 50 and of reference compounds*

| Ion | Relative ion intensities | | |
|---|---|---|---|
| | Material from fractions 41–50 | 2,4-Dimethyl-6-ethylpyridine | 2,6-Dimethyl-4-ethylpyridine |
| 135+ | 49.6 | 49.2 | 100.0 |
| 134+ | 100.0 | 100.0 | 14.9 |
| 120+ | 2.2 | 2.2 | 36.9 |
| 107+ | 26.7 | 26.7 | 5.6 |
| 91+ | 4.2 | 4.3 | 8.4 |
| 79+ | 7.3 | 6.9 | 16.0 |
| 77+ | 11.2 | 11.0 | 18.3 |

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[55] Eguchi, T., Basic Nitrogen Compounds From Fushun Shale Tar II: Bull. Chem. Soc., Japan, vol. 3, 1928, pp. 227–243.

[56] Work cited in footnote 53, p. 34.

[57] Thompson, R. B., Symon, T., and Wankat, C., Estimation of Pyrrole Nitrogen in Petroleum Distillates: Anal. Chem., vol. 24, 1952, pp. 1465–1467.

[58] Englemann, Ann., vol. 231, 1885, p. 50. (Brit. Abs., 1886, p. 258.)

[59] Siddiqui, R. H., Pyridine Series I. Attempt to Synthesize 2-Methyl-4-ethylpyridine: Jour. Indian Chem. Soc., vol. 16, 1939, pp. 410–414.

were particularly revealing because of the close agreement between the unknown and 2,4-dimethyl-6-ethylpyridine, whereas the other isomer was distinctly different. Also, the melting points of the picrates (table 25), infrared spectral data (table 24), and X-ray diffraction patterns of the picrates supported the identification of the compound as 2,4-dimethyl-6-ethylpyridine.

#### 2,3,5-TRIMETHYLPYRIDINE

Only a few of the fractions above number 50 yielded crystalline picrates. Fraction 56 gave a picrate melting at 182° to 184° C. A mass spectrum of material regenerated from this picrate showed a molecular weight of 121 and was sufficiently similar to that for 2,3,5-trimethylpyridine (table 30) to indicate that the compounds were probably the same. The identity of the unknown was established from a mixed melting point of its picrate with that of an authentic sample of 2,3,5-trimethylpyridine (table 25).

TABLE 30.—*Mass spectra of compound from fraction 56 and of 2,3,5-trimethylpyridine*

| Ion | Relative ion intensities | |
|---|---|---|
| | Material from fraction 56 | 2,3,5-Trimethylpyridine |
| 121+ | 100.0 | 100.0 |
| 120+ | 48.1 | 47.1 |
| 106+ | 24.7 | 26.4 |
| 79+ | 25.2 | 29.0 |
| 78+ | 8.3 | 6.7 |
| 77+ | 14.3 | 17.2 |

#### 2,6-DIMETHYL-4-ETHYLPYRIDINE

The principal component of fractions 59 and 60 was shown to be 2,6-dimethyl-4-ethylpyridine. A picrate from fraction 60 melted at 120.9° to 121.1° C., corresponding closely to the value for the picrate of 2,6-dimethyl-4-ethylpyridine that had been synthesized previously. The identity of the unknown was established from a mixed melting point of its picrate with an authentic sample (table 25), X-ray diffraction patterns of the picrates, mass spectra of material regenerated from the picrate and of 2,6-dimethyl-4-ethylpyridine (table 31), and an infrared spectrum of fraction 59 itself (table 24).

#### 2,3,4,6-TETRAMETHYLPYRIDINE

A picrate melting at 106° to 107° C. was obtained from fraction 81. A mass spectrum of the regenerated base showed a molecular weight of 135. A medium-sized peak at the molecular weight minus 15 and a very small peak at the molecular weight minus 29 indicated the probability of tetramethyl substitution. From the mass spectrum it seemed most likely that the compound was 2,3,4,6-tetramethylpyridine, but the spectra of the tetramethylpyridines are sufficiently similar so that positive identification by this means is difficult. X-ray diffraction patterns and mixed melting points of the picrates (table 25), as well as an infrared spectrum (table 24) of the fraction itself, confirmed the identity of the unknown as 2,3,4,6-tetramethylpyridine.

TABLE 31.—*Mass spectra of compound from fraction 60 and of 2,6-dimethyl-4-ethylpyridine*

| Ion | Relative ion intensities | |
|---|---|---|
| | Material from fraction 60 | 2,6-Dimethyl-4-ethylpyridine |
| 135+ | 100.0 | 100.0 |
| 134+ | 15.5 | 14.9 |
| 120+ | 34.5 | 36.9 |
| 107+ | 5.2 | 5.6 |
| 91+ | 6.9 | 8.4 |
| 79+ | 12.4 | 16.0 |
| 77+ | 14.5 | 18.3 |

### QUANTITATIVE ESTIMATION OF PYRIDINES

The qualitative identifications of pyridines discussed previously indicated that most of the pyridine homologs of low molecular weight were present in the naphtha. However, to determine the importance of any individual compound or particular type of substitution, information was needed as to the amount of each compound that was present. Accurate quantitative determinations of the individual compounds were not possible by the techniques available at the time this work was done, but estimates of the amounts present were made from the distillation curve of the tar bases. Plateaus on the curve were apportioned among the components qualitatively identified in individual fractions. The results are given in table 32. Although this method gave values that were only an order-of-magnitude estimation, they furnished some idea of the relative abundance of the compounds.

### IDENTIFICATION OF PYRROLES

The majority of the pyrroles, as mentioned previously, were found in the neutral naphtha. However, some of the pyrroles, particularly the more highly substituted ones, appeared in the tar-base fractions.

#### PYRROLES IN NEUTRAL NAPHTHA

The pyrroles were separated from a portion of the tar-acid-free naphtha by reaction with

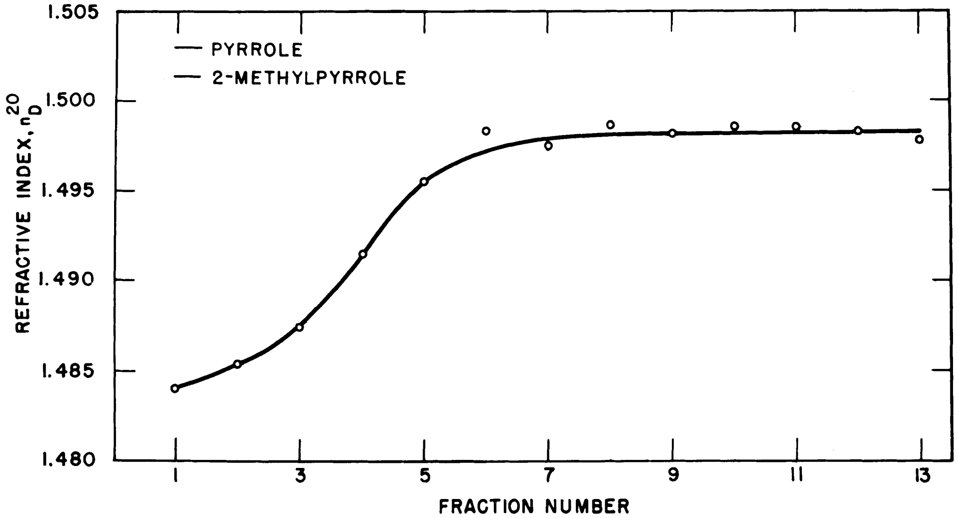

FIGURE 17.—Refractive Indices of Fractions From Distillation of Pyrroles.

TABLE 32.—*Estimated amounts of pyridines in primary N-T-U naphtha*

| Compound | Naphtha, vol.-pct. |
|---|---|
| Pyridine | Trace |
| 2-Methylpyridine | 0. 005 |
| 3-Methylpyridine | . 01 |
| 4-Methylpyridine | . 01 |
| 2,6-Dimethylpyridine | . 01 |
| 2,4-Dimethylpyridine | . 03 |
| 2,3-Dimethylpyridine | . 02 |
| 3,4-Dimethylpyridine | . 04 |
| 2,4,6-Trimethylpyridine | . 71 |
| 2,3,6-Trimethylpyridine | . 04 |
| 2,3,5-Trimethylpyridine | . 16 |
| 4-Methyl-2-ethylpyridine | . 02 |
| 2-Methyl-4-ethylpyridine | . 04 |
| 2,3,4,6-Tetramethylpyridine | . 08 |
| 2,4-Dimethyl-6-ethylpyridine | . 45 |
| 2,6-Dimethyl-4-ethylpyridine | . 17 |

solid potassium hydroxide.[60] This reaction was conducted in two stainless steel autoclaves equipped with reflux condensers and water traps on the return lines. Each vessel was charged with about 3,000 g. of naphtha. Four hundred grams of solid potassium hydroxide was supported in the naphtha on a Monel-wire screen. The reaction was run at 165° C. and 400 mm. pressure. A considerable amount of water was evolved and removed from the reaction vessel. After several days of reaction, excessive gas formation was evident, and the reaction was stopped. The naphtha was drained from the solid, tan reaction residue, which was washed with pentane and dried in a vacuum desiccator. The dried residue, containing potassium salts of the pyrrolic compounds and excess potassium hydroxide, was added to water, and the hydrolyzed pyrroles were steam-distilled. Approximately 116 ml. of a yellowish oil was obtained. The oil darkened rapidly and developed a reddish color despite being stored at −5° C. under a nitrogen atmosphere.

Sixty-eight grams of the pyrrolic material was distilled, at a reflux ratio of 20:1, in a column packed with stainless steel helices. The column was vacuum jacketed, equipped with an automatic takeoff device, and had the following dimensions: Height 30 cm., diameter 11 mm. Thirteen fractions of about 1 ml. each were obtained. The refractive indices of these fractions are shown in figure 17.

Portions of fractions 7 and 8 from the distillation were reacted with phthalic anhydride according to the method of Ciamician and Dennstedt.[61] Recrystallization yielded yellow-orange needles melting at 239° C., compared with a literature [61] value of 240° C. for pyrrole phthalate. Pyrrole phthalate prepared from Eastman Kodak Co. white-label pyrrole melted at 240° C., and a mixed melting point with the phthalate of the unknown compound was 239° C. The nitrogen content of the latter compound was 7.28 pct., compared with a theoretical value of 7.11 pct.

The remainder of fractions 7 and 8 plus all of fraction 9 were used to form the tetraiodo derivative of pyrrole according to the method of Ciamician and Silber.[62] Flaky yellow crystals were obtained that had no sharp melting point but exhibited a gradual transition, being partly melted and partly decomposed in the temperature range 140° to 150° C. Similar

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[60] Jannsen, A. G., Schierz, E. R., Van Meter, R., and Ball, J.S., Isolation and Identification of Pyrrole and 2-Methylpyrrole From Shale Oil: Jour. Am. Chem. Soc., vol. 73, 1951, pp. 4040-4041.

[61] Ciamician, G., and Dennstedt, M., Ber., vol. 17, 1884, p. 2957.

[62] Ciamician, G., and Silber, P., Ber., vol. 18, 1885, p. 1766.

melting phenomena were exhibited by the tetraiodopyrrole prepared from Eastman pyrrole. According to the literature, tetraiodopyrrole melts with decomposition in the range 140° to 150° C. The nitrogen contents of the derivatives were as follows: Calculated, 2.45 pct.; determined from shale-oil material, 2.44 pct.; determined from Eastman pyrrole, 2.40 pct.

2-Methylpyrrole was identified in a composite prepared from fractions 2 to 10. Five grams of pyrrolic material was mixed with 6 g. of hydroxylamine hydrochloride, 4 g. of anhydrous sodium carbonate, and 50 g. of 95 pct. ethanol. The mixture was refluxed for 18 hr. A pale yellow-white, crystalline material, which melted at 69° C., was obtained in the reflux condenser. The value reported in the literature[63] for the ketoxime derivative of 2-methylpyrrole is 69° to 70° C. Molecular weight of the material by the Rast cryoscopic camphor method[64] was 129.5 (calculated, 130). A nitrogen determination on the material gave 21.54 pct. (calculated, 21.52).

### PYRROLES IN TAR BASES

As was described in the pyridine identification work, the higher boiling tar-base fractions contained pyrroles as well as pyridines. In fractions 69 to 80 and 84 to 86, pyrroles were found to be the principal components. Crystals formed in these samples during refrigerated storage. The crude solids were readily recrystallized from pentane to yield colorless crystals that darkened and liquefied after exposure to air for a few hours.

Mass-spectral data on the crystalline material from fractions 69 to 80 showed a molecular weight of 123. This corresponds to an alkylpyrrole having four carbon atoms outside the ring. The mass spectrum also indicated the probable absence of any substituent group larger than methyl, suggesting that the unknown was 2,3,4,5-tetramethylpyrrole. Corroborative evidence for this identification was obtained from the melting point of the compound itself and of the picrate, as shown in table 33. The melting point of 108° to 109° C., which is unusually high for an organic compound of molecular weight 123, is strong evidence in itself for symmetrical tetrasubstitution. The styphnate of the compound obtained from shale oil melted at 112.2° to 112.8° C., which is much lower than the 159° C. given in the one reference[65] available in the literature. The preceding data cast doubt on the validity of the literature value.

The mass spectrum of the recrystallized material from fractions 84 to 86 indicated a compound having a molecular weight of 137 and at least one ethyl substituent. The melting point of the compound and that of its picrate, shown in table 33, identified the unknown as 2,4,5-trimethyl-3-ethylpyrrole.

Each of these compounds gave a negative Ehrlich's test at room temperature but a positive test when heated. Such behavior would be expected for pyrroles having substituents on all four carbon atoms. The two tetrasubstituted compounds should be more basic than less highly substituted pyrroles[66] and actually were shown to be titratable with perchloric acid so that it is not unreasonable for them to be found with the basic constituents.

TABLE 33.—*Identification of pyrroles*

| | 2,3,4,5-Tetramethylpyrrole | 2,4,5-Trimethyl-3-ethylpyrrole |
|---|---|---|
| Melting point of compound: | | |
| Found ° C. | 108-109 | 67.5-68.5 |
| Literature [1] ° C. | 110 | 69 |
| Melting point of picrate: | | |
| Found ° C. | 122.5-123.5 | 104-108 |
| Literature [1] ° C. | 127 | 104-105 |

[1] Fischer, H., and Orth, H., Die Chemie des Pyrroles: Akademische Verlagsgesellschaft M.b.H., Leipsig, 1934, Edwards Brothers, Inc., Ann Arbor, Mich., 1943, Band I, pp. 43-55.

### IDENTIFICATION OF NITRILES

During the analysis of the neutral naphtha, ultraviolet absorption spectra for some fractions exhibited peaks that could not be accounted for by the aromatics that would normally be present. For example, a fraction boiling at about 150° C. showed a peak in the ultraviolet spectrum at 2,770 A. Elution of the fractions from Florisil[67] concentrated the material giving this peak in the more strongly adsorbed portions, indicating that it was probably a nitrogen-containing compound. A mass spectrum of this concentrate showed that it contained a substance having a molecular weight of 103, which corresponds to that of benzonitrile. Peaks in an ultraviolet absorption spectrum of the concentrate were at the same wavelengths as those of known benzonitrile as shown in figure 18. The curves were obtained at different concentrations to facilitate comparison. In a similar manner, 2-methylbenzonitrile was identified in a fraction boiling at about 174° C. and 3-methylbenzonitrile in one boiling at about 184° C.

## OXYGEN COMPOUNDS

Some of the oxygen compounds in the naphtha may be extracted with aqueous

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[63] Oddo, B., and Mameli, R., Pyrrole Group XII. The Alkalation of Pyrroles. II: Gazz. Chim. Ital., vol. 44, No. 2, 1914, p. 162-174.

[64] Shriner, R. L., and Fuson, R. C., The Systematic Identification of Organic Compounds: John Wiley and Sons, Inc., New York, N.Y., 1940, p. 122.

[65] Fischer, H., and Orth, H., Die Chemie des Pyrroles: Akademische Verlagsgesellschaft M. b. H., Leipsig, 1934, Edwards Brothers, Inc., Ann Arbor, Mich., 1943, Band I, pp. 43-55.

[66] Elderfield, R. C., Heterocyclic Compounds: John Wiley and Sons, New York, N.Y., vol. 1, 1950, p. 285.

[67] Smith, J. R., Smith, C. R., and Dinneen, G. U., Separation of Nitrogen Compounds by Adsorption From Shale Oil: Anal. Chem., vol. 22, 1950, pp. 867-870.

TABLE 34.—*Identification of phenols by infrared spectroscopy*

| | Absorption peaks used for identification, wavelength in microns [1] |
|---|---|
| Phenol | 14.53, 13.33, 12.34, 12.10, 11.34, 10.02, 9.78, 9.36 |
| Fractions 1–15 | 14.53, 13.33, 12.32, 12.08, 11.34, 10.01, 9.76, 9.36 |
| 2-Methylphenol | 14.11, 13.34, 11.86, 10.83, 10.14, 9.62, 9.06 |
| Fractions 7–31 | 14.10, 13.33, 11.84, 10.81, 10.15, 9.62, 9.06 |
| 2,6-Dimethylphenol | 13.71, 13.12, 12.12, 11.00, 9.80, 9.19, 9.07 |
| Fractions 25–39 | 13.71, 13.12, 12.12, 11.00, 9.80, 9.19, 9.06 |
| 4-Methylphenol | 13.52, 12.23, 11.87, 9.85, 9.06 |
| Fractions 29–59 | 13.51, 12.23, 11.87, 9.85, 9.06 |
| 3-Methylphenol | 14.58, 12.89, 11.71, 10.75, 9.99, 9.60, 9.24 |
| Fractions 30–61 | 14.57, 12.89, 11.71, 10.75, 10.01, 9.61, 9.24 |
| 2-Ethylphenol | 13.68, 13.35, 10.40, 9.01 |
| Fractions 34–60 | 13.65, 13.34, 10.40, 9.00 |
| 2,4-Dimethylphenol | 13.00, 12.48, 12.29, 11.45, 10.77, 9.91, 9.68 |
| Fractions 57–70 | 13.01, 12.48, 12.29, 11.45, 10.75, 9.89, 9.68 |
| 2,5-Dimethylphenol | 11.85, 11.58, 10.07, 9.01 |
| Fractions 58–70 | 11.85, 11.58, 10.06, 9.01 |
| 2, 3-Dimethylphenol | 14.14, 13.01, 12.28, 11.10, 10.12, 9.82, 9.40, 9.15 |
| Fractions 66–72 | 14.15, 13.02, 12.28, 11.10, 10.11, 9.82, 9.41, 9.16 |
| 4-Ethylphenol | 12.08, 9.60, 9.02 |
| Fractions 66–72 | 12.07, 9.60, 9.01 |
| 2,4,6-Trimethylphenol | 13.72, 11.70, 10.78, 9.85 |
| Fractions 71–72 | 13.71, 11.70, 10.78, 9.85 |

[1] Only clearly defined peaks were used in identifications. Peaks that were obscured by other components, or that were not definite because of low concentration of the identified compound, are not shown.

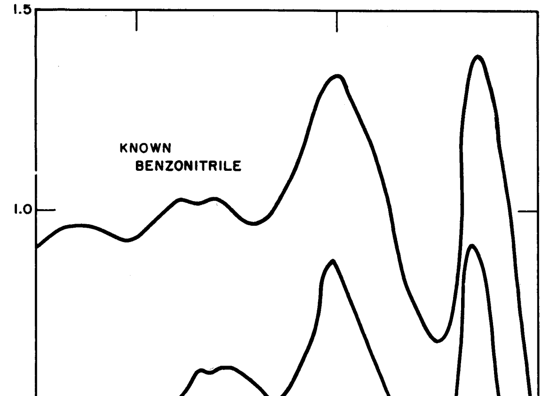

FIGURE 18.—Ultraviolet Spectra for Benzonitrile.

reagents, while some remain in the raffinate. Therefore, the identification of oxygen compounds required work on both the tar-acid extract and the neutral oil.

## ACIDIC MATERIAL

### PHENOLS

The aqueous sodium hydroxide solution containing tar acids as sodium salts was divided into several 4-l. batches, each of which was treated with one 500-ml. and two 250-ml. portions of ethyl ether to recover occluded oil. The washed batches were recombined and the pH adjusted to a value of 8.0 with 50 pct. sulfuric acid. Free phenols separated as an upper layer, whereas carboxylic acids remained in solution as sodium salts. The water layer was extracted with solvent to remove dissolved phenols. A total of 975 g. of dried, crude phenols was recovered.

The crude phenols were distilled through a Stedman screen-packed column, described previously, to give 72 fractions of approximately 10 ml. each. The qualitative and quantitative analysis of these fractions was based on infrared spectra.

Infrared spectra for the fractions were determined over the wave-length region of 8.0 to 15.0 $\mu$. The compounds occurring in each fraction were identified from a comparison of these spectra with those of known compounds. Qualitative indications of the presence of 11 phenols were obtained. Table 34 gives a list of these, the fractions in which they were identified, and the wavelength of the absorption peaks used for identification.

The composition of each fraction was determined by the infrared absorption method of Friedel and coworkers.[68] From these data the composition of the crude phenols was calculated. The results are shown in table 35. No attempt was made to identify the com-

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[68] Friedel, R. A., Pierce, L., and McGovern, J. J., Infrared Analysis of Phenols, Cresols, Xylenols, and Ethylphenols: Anal. Chem., vol. 22, 1950, pp. 418–420.

TABLE 35.—*Composition of phenolic portion of the tar acids from primary N–T–U naphtha, in volume-percent*

| Compound | Crude phenols | Raw naphtha |
|---|---|---|
| Phenol | 11.7 | 0.16 |
| 2-Methylphenol | 19.2 | .27 |
| 3-Methylphenol | 10.9 | .15 |
| 4-Methylphenol | 18.8 | .26 |
| 2-Ethylphenol | 1.5 | .02 |
| 4-Ethylphenol | .7 | .01 |
| 2,3-Dimethylphenol | 4.3 | .06 |
| 2,4-Dimethylphenol | 7.5 | .11 |
| 2,5-Dimethylphenol | 2.9 | .04 |
| 2,6-Dimethylphenol | 5.6 | .08 |
| 2,4,6-Trimethylphenol | .1 | Trace |
| Residue | 16.8 | .23 |
| Total | 100.0 | 1.39 |

ponents in the higher boiling residue. In considering the relative abundance of the various compounds, it should be remembered that only two of these phenols boil below the nominal cut point (200° C.) of the naphtha. However, possible effects of azeotropic distillation and lack of sharp fractionation during the naphtha-production distillation resulted in the presence of some phenols boiling above this temperature.

### CARBOXYLIC ACIDS

The solution from which phenols had been removed was treated further with sulfuric acid to a pH 0.7. Cloudiness developed, but there was no phase separation. The aqueous material was extracted with ethyl ether, and the latter was subsequently distilled off, leaving 36 ml. of dark brown liquid residue. Titration for acidic oxygen content showed both carboxylic and phenolic types of oxygen present. Ultraviolet-spectral examination confirmed the presence of phenols.

The crude acids were redissolved in a slight excess of aqueous 10-pct. sodium hydroxide. Fractional release of the dissolved materials was carried out, using several decreasing pH steps, in an attempt to secure clean-cut separation of phenols from carboxylic acids. The pH steps used in this procedure were: 10.5, 9.0, 7.5, 6.2, 4.0, and 1.0. Phenols were predominant in materials released at pH levels of 10.5, 9.0, and 7.5. They were present in appreciable quantities in materials released at pH levels of 6.2 and 4.0. The material recovered by lowering the pH from 4.0 to 1.0 was free of phenols.

Examination of the material recovered at pH levels of 6.2 and 4.0 showed that in addition to phenols, it contained sodium salts of carboxylic acids. The organic acids were released from these salts by treating the mixture with dilute sulfuric acid. The mixture of phenols and carboxylic acids, amounting to about 8.5 g., was distilled through a microcolumn packed with metal helices to yield five overhead fractions and a residue:

| *Fraction* | *Boiling range (585 mm.), ° C.* |
|---|---|
| 1 | 90–170 |
| 2 | 170–190 |
| 3 | 190–201 |
| 4 | 201–206 |
| 5 | 206–209 |
| Residue | |

Ultraviolet-spectral examination of fractions 2 through 5 showed that 2 and 3 contained large amounts of phenols, 4 contained some, and 5 contained only a trace. Mass-spectral examination confirmed the presence of phenols in the first fractions and gave evidence that fractions 4 and 5 and the residue contained $C_6$-, $C_7$-, and $C_8$-carboxylic acids. Saturated acids appeared to predominate.

A small portion of fraction 5 was paper-chromatographed in a series of runs where its migration behavior was compared with that of known carboxylic acids. The only prominent spot produced by the shale-oil material invariably corresponded to the migration of n-heptanoic acid. The amide derivative of fraction 5 melted at 91° to 92° C., and that of n-heptanoic acid melted at 94.5° to 95.0° C. A mixture of the two amides melted at 93.5° to 94.5° C. Thus, the presence of n-heptanoic acid in fraction 5 was established. The $C_6$- and $C_8$-acids suggested by mass-spectral examination were apparently present in too low a concentration to be detected by the paper-chromatography and amide-formation techniques.

About 7.4 g. of the acids liberated within the pH range 4.0 to 1.0 was also distilled through the microcolumn to yield four overhead fractions and a residue:

| *Fraction* | *Boiling range (585 mm.), ° C.* |
|---|---|
| 1 | 85–160 |
| 2 | 160–190 |
| 3 | 190–195 |
| 4 | 195–197 |
| Residue | |

Mass spectra of the above fractions suggested that $C_6$-, $C_7$-, and $C_8$-acids were present and that unsaturated acids predominated. No individual compound was identified in these fractions.

The severe contamination of carboxylic acid concentrates with phenols suggested that phenolic concentrates might contain carboxylic acids. A portion of the crude phenols discussed in the previous section was dissolved in aqueous 10-pct. sodium hydroxide. The pH of the solution was lowered to 9.0 by addition of mineral acid, and the liberated phenols were removed from the mother liquor by solvent extraction. The pH was then lowered to 0.5 and the mother liquor again extracted to yield a product containing both phenols and carboxylic acids. This was treated with sodium methoxide in methanol followed by dimethyl sulfate to etherify phenols. After reflux to drive the reaction to equilibrium, the excess methanol was distilled off and water was added. Phenyl ethers were extracted, and the aqueous layer was then treated with mineral acid to free the carboxylic acids. The resulting product was enriched with respect to carboxylic acids but still contained phenols. It was treated with diazomethane in the following five-step process to eliminate phenols completely:

(1) The mixture was reacted with diazomethane to esterify the carboxylic acids quantitatively. Some phenols were etherified.

(2) The unreacted phenols were removed from the reaction mixture by extraction with aqueous caustic.

(3) The raffinate was boiled with additional aqueous caustic to hydrolyze esters. Phenyl ethers did not react.

(4) The hydrolysis mixture was extracted with an organic solvent to remove phenyl ethers.

(5) The raffinate from preceding step was acidified with mineral acid to yield phenol-free carboxylic acids.

A portion of the product from the purification was reacted with p-bromophenacyl bromide. The resulting crop of needlelike crystals was recrystallized from ethanol. They melted at 116.7° to 117.7° C. The corresponding derivative of benzoic acid melted at 117.2° to 118.2° C. A mixture of the two derivatives melted at 116.7° to 118.2° C., indicating identity. Thus, benzoic acid was identified as a constituent of the carboxylic acids from shale-oil naphtha.

Benzoic acid was also identified during some preliminary work on the crude carboxylic acids first obtained from the naphtha. A solid crystallizing from these acids had an ultraviolet absorption spectrum identical with that of benzoic acid. Melting points of the unknown and its anilide and mixed melting points with authentic materials confirmed the identification. The melting point data are as follows:

| Material | Melting point, ° C. | |
|---|---|---|
| | Free acid | Anilide |
| Unknown | 122–122. 5 | 162. 5–162. 8 |
| Benzoic acid | 124–125. 5 | 163. 5–163. 8 |
| Mixture | 123–124 | 163. 0–164. 0 |

### NONACIDIC MATERIAL

Ultraviolet spectra were obtained on the fractions from distillation of the neutral naphtha as part of the examination of these fractions for aromatic compounds. The spectrum of a fraction boiling at 162° C. showed a peak at 2,805 A. that could not be attributed to the alkyl benzenes boiling in that range. The unknown compound was concentrated by adsorption of the fraction on silica gel and elution with pentane. The hydrocarbons in the fraction were eluted first, followed by material rich in the compound exhibiting the unique peak. A mass spectrum indicated the compound had a molecular weight of 118 and no easily removed methyl groups, as the 103 peak was very small. Comparison of the mass and ultraviolet spectra of the unknown with those of an authentic sample of benzofuran, table 36 and figure 19, showed that the compounds were identical.

TABLE 36.—*Selected peaks from the mass spectra of known and isolated benzofuran*

| Ion [1] | Relative ion intensities | |
|---|---|---|
| | Known benzofuran | Isolated benzofuran |
| 119+ | 9. 6 | 9. 8 |
| 118+ | 100. 0 | 100. 0 |
| 91+ | 4. 0 | 4. 9 |
| 90+ | 42. 1 | 42. 3 |
| 89+ | 40. 0 | 39. 0 |

[1] Due to presence of n-pentane in the isolated material, peaks below 72 could not be compared readily.

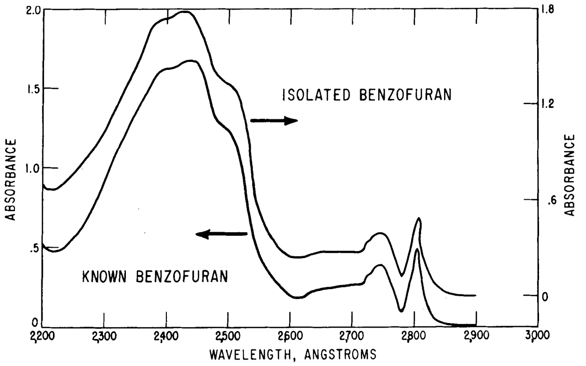

FIGURE 19.—Ultraviolet Spectra for Benzofuran.

## PUMPHERSTON NAPHTHA

The naphtha was obtained from a crude oil produced from Green River shale in a Pumpherston retort during Bureau of Mines oil-shale operations in the period 1925–1929.[69] [70] The naphtha was prepared in this laboratory by batchwise distillation of the oil, using a 12-l. flask equipped with Claissen head and Glas-

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[69] Gavin, M. J., and Desmond, J. S., Construction and Operation of the Bureau of Mines Experimental Oil-Shale Plant, 1925-27: Bureau of Mines Bull. 315, 1930, 154 pp.

[70] Cattell, R. A., Guthrie, Boyd, and Schramm, L. W., Retorting Colorado Shale Oil—A Review of the Work of the Bureau of Mines, U.S. Department of the Interior: Oil Shale and Cannel Coal, vol. 2, Inst. Petrol., London, 1951, pp. 345-398.

col heating mantle.[71] For each batch, a 7-l. charge was distilled under nitrogen at atmospheric pressure (585 mm. of mercury) until water ceased to come over. Approximately 118 ml. of naphtha and 22 ml. of water were obtained below a vapor temperature of 135° C. from each charge. The absolute pressure was reduced to about 10 mm. of mercury, and the distillation continued, using a steady, small stream of nitrogen to prevent bumping. The vacuum distillation yielded an average of 1,245 ml. of product from each charge below a cut temperature of 90° C. The combined distillates, free of water, were stored in brown bottles at 0° C., over anhydrous sodium sulfate, under an atmosphere of nitrogen. The properties of the 13.7 l. of dry naphtha obtained by this procedure from 69.3 l. of crude shale oil are shown in table 37.

TABLE 37.—*Properties of raw Pumpherston naphtha*

| | |
|---|---|
| Specific gravity, 15.6°/15.6° C. | 0. 805 |
| Gravity °API. | 44. 3 |
| ASTM distillation at 760 mm.: | |
| 10 percent ° C.. | 151 |
| 50 percent ° C.. | 176 |
| 90 percent ° C.. | 221 |
| Sulfur weight-percent. | 0. 84 |
| Nitrogen do | . 51 |

Tar acids were removed from the naphtha, which was saturated with nitrogen, by extraction with three successive portions of aqueous 20-pct. sodium hydroxide solution, also saturated with nitrogen. This strength of reagent was used in early work before investigation had shown that 10-pct. reagents generally gave better results. The caustic solution was in turn washed with ether to recover occluded oil. The ether was removed by distillation and the residue returned to the naphtha raffinate. The aqueous caustic was acidified by the addition of dilute sulfuric acid. Properties of the 83.4 g. of crude tar acids are shown in table 38.

Tar bases were removed from the tar-acid-free naphtha by extraction with three successive portions of aqueous 20-pct. sulfuric acid, saturated with nitrogen. The acid solution was in turn washed with ether to recover occluded oil. However, evaporation of the ether gave only a semisolid sludge, so it was not added to the remainder of the neutral oil. The aqueous acidic solution was made basic with sodium hydroxide to liberate the tar bases. The properties of the 610 g. of product thus obtained are also shown in table 38.

TABLE 38.—*Properties of tar acids and tar bases extracted from Pumpherston naphtha*

| | Tar acids | Tar bases |
|---|---|---|
| Specific gravity, 15.6°/15.6° C. | 0. 9750 | 0. 9490 |
| Gravity ° API. | 13. 6 | 17. 6 |
| Refractive index, $n_D^{20}$ | 1. 4887 | 1. 5007 |
| Sulfur weight-percent. | 0. 18 | 0. 20 |
| Nitrogen do | . 08 | 5. 06 |

TABLE 39.—*Hydrocarbons in neutral Pumpherston naphtha*

| | Volume-percent |
|---|---|
| Paraffins: | |
| n-Hexane | 0. 1 |
| Methylhexanes | . 2 |
| n-Heptane | . 2 |
| Dimethylhexanes | . 3 |
| Methylheptanes | . 2 |
| n-Octane | 1. 6 |
| Dimethylheptanes | . 6 |
| Methyloctanes | . 5 |
| n-Nonane | 3. 4 |
| Other $C_{10}$-paraffins | 2. 2 |
| n-Decane | 4. 1 |
| Higher boiling compounds | 9. 3 |
| Total | 22. 7 |
| Cycloparaffins: | |
| $C_6$-cycloparaffins | . 03 |
| Methylcyclohexane | . 03 |
| Ethylcyclopentane | . 04 |
| 1,2,4-Trimethylcyclopentane | . 1 |
| Other $C_8$-cycloparaffins | . 7 |
| $C_9$-cycloparaffins | 2. 1 |
| $C_{10}$-cycloparaffins | 1. 6 |
| Higher boiling compounds | 4. 2 |
| Total | 8. 8 |
| Aliphatic olefins: | |
| n-Heptenes | . 7 |
| n-Octenes | 2. 5 |
| Branched nonenes | 1. 1 |
| n-Nonenes | 4. 2 |
| Branched decenes | 1. 9 |
| n-Decenes | 4. 3 |
| Higher boiling compounds | 13. 0 |
| Total | 27. 7 |
| Cycloolefins: | |
| $C_6$-cycloolefins | . 1 |
| $C_7$-cycloolefins | . 5 |
| $C_8$-cycloolefins | 1. 4 |
| $C_9$-cycloolefins | 3. 2 |
| $C_{10}$-cycloolefins | 2. 6 |
| Higher boiling compounds | 8. 3 |
| Total | 16. 1 |
| Aromatics: | |
| Benzene | . 2 |
| Toluene | 1. 1 |
| Ethylbenzene | . 3 |
| p-Xylene | . 7 |
| m-Xylene | 1. 6 |
| o-Xylene | 9 |
| 1-Methyl-3-ethylbenzene | . 8 |
| 1-Methyl-4-ethylbenzene | . 4 |
| 1-Methyl-2-ethylbenzene | . 9 |
| 1,3,5-Trimethylbenzene | |
| 1,2,4-Trimethylbenzene | 1. 5 |
| 1,2,3-Trimethylbenzene | 1. 8 |
| 1-Methyl-2-isopropylbenzene | |
| 1-Methyl-3-isopropylbenzene | |
| 1-Methyl-4-isopropylbenzene [1] | |
| Higher boiling compounds | 9. 2 |
| Total | 19. 4 |
| Grand total | 94. 7 |

[1] Most probable compound based on ultraviolet spectra.

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[71] Ball, J. S., Dinneen, G. U., Smith, J. R., Bailey, C. W., and Van Meter, R., Composition of Colorado Shale-Oil Naphtha: Ind. Eng. Chem., vol. 41, 1949, pp. 581-587.

## HYDROCARBON COMPOUNDS

Analysis of the neutral naphtha was less comprehensive than that described for the N-T-U naphtha, but the approach was similar. A 4-l. charge of the naphtha was distilled at atmospheric pressure through a column packed with stainless steel helices. The column had the following dimensions: Height, 9 ft; diameter, 1 in. The distillation yielded 105 fractions, each containing 20 ml., and a residue. The following properties were determined on each of the fractions: Boiling point at a pressure of 760 mm. of mercury; density at 20° C.; refractive indices for the sodium *D* and mercury *g* lines at 20° C.; sulfur content; nitrogen content; hydrocarbon groups by silica-gel-adsorption analysis; and an ultraviolet-absorption spectrum. Results of the hydrocarbon-group analyses of the fractions are shown in figure 20. From the data, the quantity of each type of compound distilled during each degree rise in vapor temperature was calculated, as described previously for N-T-U naphtha. The results of these calculations for the hydrocarbons in the naphtha are shown in figure 21. For ready reference, a number of hydrocarbons found in shale oil are shown at their boiling points. The peaks in figure 21 indicate definite segregation of groups of isomers or even, in some instances, of individual compounds. From the areas under these peaks, quantities present in the naphtha were estimated. The results are given in table 39.

At the time that the work on this naphtha was done, there was particular interest in whether or not the use of silica gel in chromatographic procedures caused appreciable analytical errors due to polymerization of olefins. Conversion of olefins to the corresponding paraffins or cycloparaffins by hydrogenation offered a possibility of substantiating the results for olefins calculated from analyses of the fractions from the distillation of the neutral naphtha. Inasmuch as the saturates could be identified more readily than the olefins, information could be obtained regarding the original carbon structure of the unsaturated molecule if no rearrangements occurred during hydrogenation. Mild conditions were used to reduce the probability of such rearrangements.

A sample of neutral naphtha was hydrogenated, using Raney nickel as a catalyst at an initial pressure of 500 p.s.i.g. and a tempera-

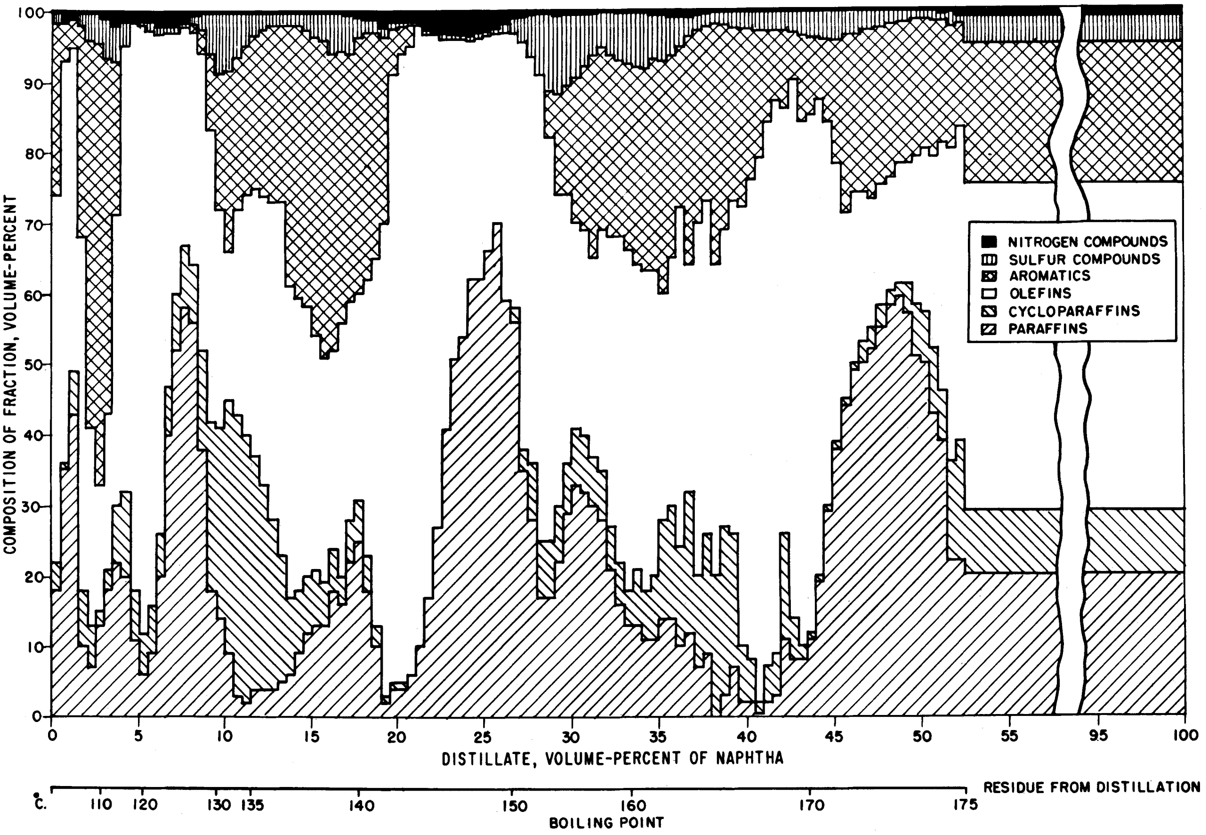

FIGURE 20.—Amounts of Various Classes of Compounds in Each Fraction From Distillation of Neutral Pumpherston Naphtha.

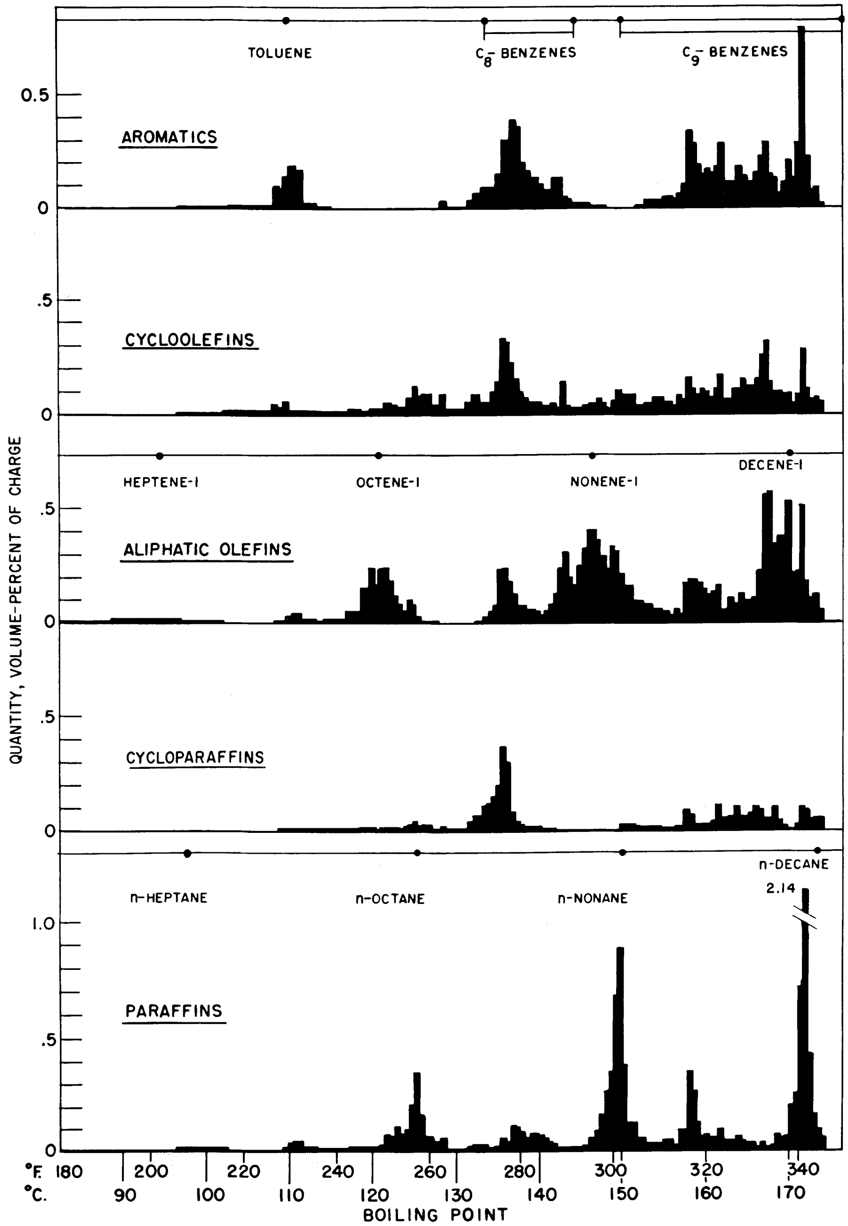

FIGURE 21.—Amounts of Various Classes of Hydrocarbons in Neutral Pumpherston Naphtha.

ture of 150° C. Seven successive batch operations were necessary to hydrogenate all of the olefins. The saturated portion of the hydrogenated naphtha was separated from the aromatic portion by adsorption on silica gel. Pentane was used as the eluent for the saturates, and the aromatics were desorbed with 2-propanol. A sample of the saturates was distilled to give fractions containing 10 ml. each (0.5 vol.-pct.), on which the following properties were determined: Boiling point at 760 mm. pressure; refractive indices for the sodium *D* and mercury *g* lines at 20° C.; and density at 20° C.

The quantity distilled per degree rise in temperature was calculated, as described previously, for the paraffins and cycloparaffins and used to estimate the quantities of compounds present. These quantities include compounds from two sources: The saturates present in the original naphtha and those resulting from hydrogenation of the olefins. The differences between the values for the hydrogenated and original naphthas represent the olefins.

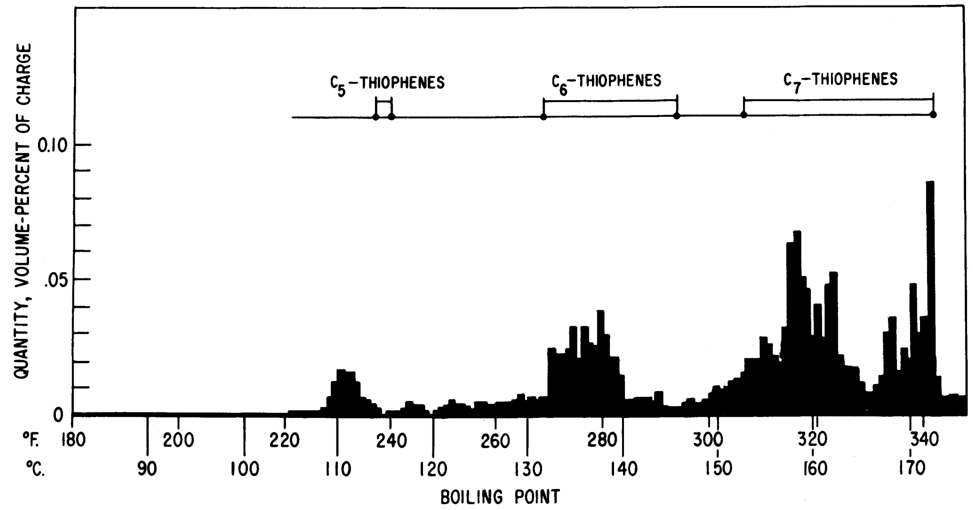

Figure 22.—Amounts of Sulfur Compounds in Neutral Pumpherston Naphtha.

Table 40 gives the results for olefins obtained from the hydrogenated sample and from distillation of the original sample. Excellent agreement is shown between the totals obtained by the two methods for the aliphatic olefins. Some variations in the values for individual groups are evident. These may be caused by overlapping of the boiling ranges of the various groups. The results for cyclic olefins calculated from the hydrogenated sample are somewhat higher than those from the original naphtha. This is apparently due to some hydrogenation of the aromatics, which were reduced from 19 to 15 pct. in the operation.

Table 40.—*Comparison of olefin contents calculated from neutral naphtha and from hydrogenated naphtha, in volume-percent*

| | Original sample | Hydrogenated sample |
|---|---|---|
| Aliphatic olefins: | | |
| Heptenes | 0.7 | 0.8 |
| Octenes | 2.5 | 2.4 |
| Branched nonenes | 1.1 | 1.0 |
| n-Nonenes | 4.2 | 3.1 |
| Branched decenes | 1.9 | 2.2 |
| n-Decenes | 4.3 | 4.8 |
| Total | 14.7 | 14.3 |
| Cycloolefins: | | |
| $C_6$-cycloolefins | .1 | .1 |
| $C_7$-cycloolefins | .5 | .8 |
| $C_8$-cycloolefins | 1.4 | 2.3 |
| $C_9$-cycloolefins | 3.2 | 4.8 |
| $C_{10}$-cycloolefins | 2.6 | 2.9 |
| Total | 7.8 | 10.9 |

## NONHYDROCARBON COMPOUNDS

Nonhydrocarbon compounds comprised about 5 pct. of the neutral naphtha in addition to being the principal constituents in the extracted tar acids and tar bases. Consequently, some work was done on all three of these materials.

An analysis for types of sulfur compounds was made on the neutral naphtha with the results shown in table 41. As mentioned under the N–T–U work, the method used[72] is not readily applicable to highly unsaturated materials, so the results should be considered only as approximations. However, they are in general agreement with the results found on the N–T–U naphtha, as the residual sulfur classification, which would contain the thiophenes, comprises about two-thirds of the sulfur. Some additional evidence for the presence of thiophenes is indicated in figure 22, which is a plot for sulfur compounds similar to those described previously for hydrocarbons. Peaks shown in the figure agree quite well with the boiling ranges of thiophenes.

The tar bases recovered from the aqueous acid were examined in an effort to identify individual components. A 98.5-g. charge of the bases was distilled at a pressure of 100 mm. of mercury through a column packed with stainless steel helices. The column dimensions

Table 41.—*Group sulfur analysis of neutral Pumpherston naphtha*

| Sulfur type | Sulfur present as indicated type, wt.-pct. |
|---|---|
| Free sulfur | 0 |
| Thiol | 0 |
| Disulfide | 7 |
| Sulfide | 24 |
| Residual (including thiophene) | 69 |

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[72] Ball, John S., Determination of Types of Sulfur Compounds in Petroleum Distillates: Bureau of Mines Rept. of Investigations 3591, 1941, 60 pp.

were: Height, 2 ft; diameter, 0.5 in. Eighty-two distillate fractions, each containing about 1 ml., were obtained. Ultraviolet spectra, the only type for which equipment was available when this work was done, indicated the presence of 2-methylpyridine, 2,4,6-trimethylpyridine, quinoline, and 2-methylquinoline in some of the fractions.

The tar acids were investigated for the presence of phenols and carboxylic acids. The crude tar acids were dissolved in aqueous 5-pct. sodium hydroxide, and the phenols were liberated from this solution by saturation with carbon dioxide. Subsequent acidification of the mother liquor yielded about 1 g. of material free from the typical phenol odor. This material was probably carboxylic acids, as an ultraviolet spectrum showed no evidence of aromatic compounds. Owing to the small amount of material available, no attempt was made to separate and identify individual compounds.

A 52.5-g. charge of the phenols liberated by carbon dioxide treatment was distilled in a semimicro column at a pressure of 100 mm of mercury. Phenol and 4-methylphenol were identified in certain of the distillation fractions from a comparison of ultraviolet spectra as illustrated in figure 23. These were the only fractions in which a single compound was present in sufficient concentration to permit this type of identification. At the time that this work was done, facilities for obtaining infrared spectra were not available, so analyses similar to those described for the N–T–U naphtha were not possible.

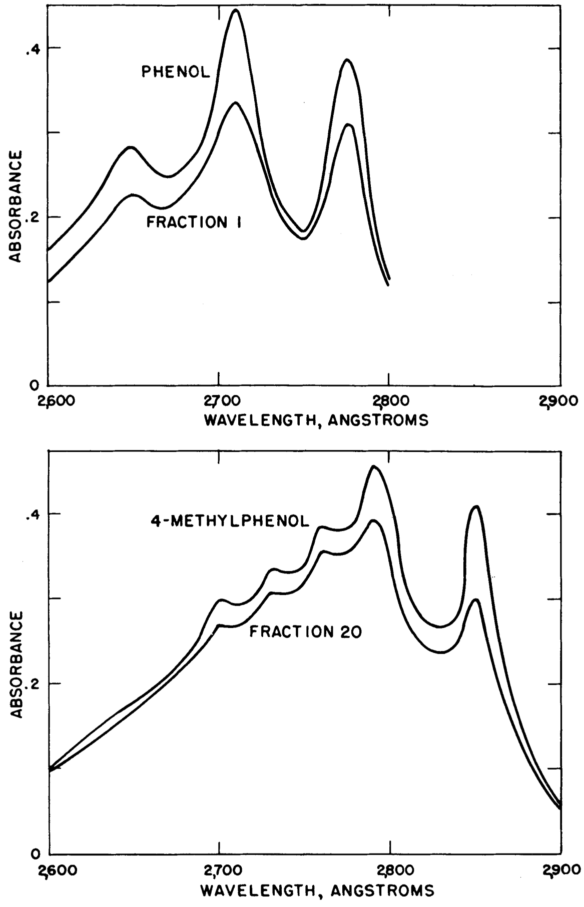

Figure 23.—Ultraviolet Spectra of Selected Tar-Acid Fractions Compared With Reference Compounds.

## HAYES NAPHTHA

The Hayes retort was operated in the summer of 1946 in cooperation with the Colorado Fuel and Iron Corp. at Pueblo, Colo.[73] The retort had been designed as a low-temperature coal-carbonization pilot plant and was applied to shale in a short-term experimental operation. During part of the operation a highly aromatic oil was produced, presumably as the result of high retorting temperature. As no extensive evaluation of this retort was planned, a comprehensive investigation of the oil was not made. However, the distribution of individual aromatic compounds boiling below 150° C. was determine to compare it with that in oils retorted at lower temperatures.

A naphtha cut was removed from about 3,400 ml. of the crude oil by a simple distillation. Tar acids and tar bases, amounting to 0.2 pct. and 10.2 pct., respectively, were extracted from the naphtha. A charge of 532 ml. of the neutral naphtha was distilled, and 10-ml. fractions were taken. Thirty-one fractions were obtained below a vapor temperature of 150° C. A hydrocarbon-group analysis, sulfur

Table 42.—*Composition of neutral .Hayes distillate, in volume-percent*

| Compound or class | Distillate boiling below 150° C. | Crude oil |
|---|---|---|
| Benzene | 27.2 | 3.13 |
| Toluene | 33.5 | 3.85 |
| Ethylbenzene | 1.8 | .21 |
| p-Xylene | 3.0 | .35 |
| m-Xylene | 12.8 | 1.47 |
| o-Xylene | 4.3 | .49 |
| Styrene | 1.6 | .18 |
| Total aromatic hydrocarbons | 84.2 | 9.68 |
| Thiophene | .3 | .03 |
| Methylthiophenes | .9 | .10 |
| $C_6$-thiophenes | .8 | .09 |
| Nitrogen compounds | 1.3 | .15 |
| Cycloolefins | 2.6 | .30 |
| Aliphatic olefins | 5.2 | .60 |
| Cycloparaffins | 1.3 | .15 |
| Paraffins | 3.4 | .39 |
| Grand total | 100.0 | 11.49 |

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[73] Work cited in footnote 70, p. 41.

TABLE 43.—*Properties of wide-boiling fractions obtained from 1,200° and 1,500° F. crude shale oils*

| Description of sample | Yield | | Density at 20° C. | Viscosity, CS | | Sulfur, wt.-pct. | Nitrogen, wt.-pct. | | Sediment, wt.-pct. | Ash, wt.-pct. |
|---|---|---|---|---|---|---|---|---|---|---|
| | Weight-percent | Volume-percent | | 100° F. | 210° F. | | Total | Basic | | |
| Crude oil from 1,200° F. run | ------ | ------ | 0.9554 | 6.4 | ------ | 0.84 | 2.46 | 1.28 | ------ | ------ |
| Fraction 1, up to 150° C | 27.1 | 32.5 | .7966 | ------ | ------ | .79 | .55 | .28 | ------ | ------ |
| Fraction 2, 150° to 280° C | 20.3 | 21.0 | .9239 | ------ | ------ | .80 | 2.35 | 1.64 | ------ | ------ |
| Fraction 3, 280° to 540° C | 14.1 | 13.4 | 1.0025 | 46.3 | 4.3 | .80 | 3.30 | 1.80 | ------ | ------ |
| Fraction 4, residuum | 37.3 | 32.5 | 1.0972 | ------ | ------ | .79 | 3.54 | 1.70 | 5.5 | 1.5 |
| Crude oil from 1,500° F. run | ------ | ------ | 1.0623 | 10.9 | ------ | .75 | 3.08 | 1.29 | ------ | ------ |
| Fraction 1, up to 150° C | 26.2 | 31.8 | .8734 | ------ | ------ | .72 | .80 | .55 | ------ | ------ |
| Fraction 2, 150° to 280° C | 19.2 | 20.4 | 1.0014 | ------ | ------ | .78 | 3.32 | 2.06 | ------ | ------ |
| Fraction 3, 280° to 540° C | 17.5 | 17.1 | 1.0894 | 25.1 | 3.2 | .78 | 4.11 | 2.17 | ------ | ------ |
| Fraction 4, residuum | 37.0 | 31.3 | 1.2565 | ------ | ------ | .74 | 3.99 | .95 | 37.3 | 1.8 |

and nitrogen contents, and an ultraviolet spectrum were obtained on each fraction. The composition of the distillate boiling below 150° C. was calculated from these data, and the results are given in table 42. As with naphthas from other oils produced at higher-than-normal temperatures, there is a large relative concentration of the simpler members, benzene and toluene, of the homologous series.

## NAPHTHAS FROM HIGH-TEMPERATURE SHALE OILS

The data presented in this section resulted from a detailed characterization study of shale oils produced at 1,200°, 1,500°, and 1,700° F.[74] [75] Because the investigation was concerned with the total oil, the analytical work was conducted in a somewhat different manner from that described for the preceding naphthas. No naphtha fraction as such was obtained, so the results are reported only on the basis of the crude oil, and compounds boiling below about 220° C. are included.

The quantities available for analysis amounted to about 2.5 l. for the 1,200° F. oil, 2 l. for the 1,500° F. oil, and 0.8 l. for the 1,700° F. oil. Because of the small quantity of 1,700° F. oil, the scheme of analysis used on it differed from that used for the other two oils. The 1,200° and 1,500° F. oils were distilled into four wide-boiling cuts using a 5-l. flask equipped with a Claissen head packed to a depth of several inches with glass beads. To reduce the tendency for cracking to occur, fractions 2 and 3, table 43, were distilled at pressures of 40 and 1 mm. of mercury, respectively.

Properties of the crude oils and fractions are shown in table 43. The oils have similar boiling-range distributions, but their chemical compositions are quite different, as indicated by differences in densities and viscosities. The sulfur contents of the two oils and of the fractions from them show only minor differences. The distribution of total and basic nitrogen with respect to boiling range is different. The sediment values shown in the table represent the mineral and carbonaceous matter that was insoluble in benzene.

For the 1,200° and 1,500° F. oils, all of the compounds of interest to this report were contained in the first and part of the second fraction, so only the analysis of these will be described. Each of the first two fractions was extracted with 10 pct. aqueous sodium hydroxide to remove acidic materials and then with 10 pct. aqueous sulfuric acid to remove basic constituents. The raffinate oil was neutralized with dilute caustic and washed with distilled water. The tar acids and tar bases were liberated from the aqueous solutions by the techniques described previously, recovered, and reserved for analysis. The yields of tar acids and tar bases and some properties of the neutral oils are shown in table 44. The fractions from the 1,500° F. oil are more aromatic than those from the 1,200° F. oil. The sulfur contents of the neutral oils from the second fractions are higher than those of the raw fractions because of the removal of large quantities of tar bases that are low in sulfur. The nitrogen results in table 44 show that dilute-acid extraction was effective in removing the basic nitrogen from the first fractions but not from the second fractions. It has been found previously that effectiveness of extraction decreases in higher boiling materials. The nitrogen results on the raw fractions in table 43 and on the neutral distillates in table 44 are not directly comparable.

## HYDROCARBON COMPOUNDS

The neutral oils from the wide-boiling fractions were subjected to an analytical distillation. The distillation of the material boiling up to 150° C. was made at atmospheric pressure, about 585 mm. of mercury. The material boiling between 150° and 280° C. was distilled at reduced pressure to reduce the possibility

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[74] Brantley, F. E., Cox, R. J., Sohns, H. W., Barnet, W., I., and Mruphey, W. I. R., High Temperature Shale Oil, Production and Utilization: Ind. Eng. Chem., vol. 44, 1952, pp. 2641–2647.

[75] Dinneen, G. U., Smith, J. R., and Bailey, C. W., High Temperature Shale Oil, Product Composition: Ind. Eng. Chem., vol. 44, 1952, pp. 2647–2650.

TABLE 44.—*Yields of tar acids, tar bases, and neutral oil from first two fractions of 1,200° and 1,500° F. crude shale oils and some properties of the neutral oils*

| Description of sample | Yield, vol.-pct. | | Sulfur, wt.-pct. | Nitrogen, wt.-pct. | | Hydrocarbon analysis, vol.-pct. | | |
|---|---|---|---|---|---|---|---|---|
| | Fraction | Crude oil | | Total | Basic | Saturates | Olefins | Aromatics plus S and N compounds |
| Fraction 1 from 1,200° F. oil: | | | | | | | | |
| Tar acids | 0.5 | 0.2 | | | | | | |
| Tar bases | 2.6 | .8 | | | | | | |
| Neutral oil | 96.9 | 31.5 | 0.71 | 0.16 | 0.00 | 19 | 35 | 46 |
| Fraction 2 from 1,200° F. oil: | | | | | | | | |
| Tar acids | 3.5 | .7 | | | | | | |
| Tar bases | 17.0 | 3.6 | | | | | | |
| Neutral oil | 79.5 | 16.7 | .95 | .80 | .06 | 8 | 23 | 69 |
| Fraction 1 from 1,500° F. oil: | | | | | | | | |
| Tar acids | 1.6 | .5 | | | | | | |
| Tar bases | 5.3 | 1.7 | | | | | | |
| Neutral oil | 93.1 | 29.6 | .74 | .17 | .00 | 1 | 4 | 95 |
| Fraction 2 from 1,500° F. oil: | | | | | | | | |
| Tar acids | 1.3 | .3 | | | | | | |
| Tar bases | 21.2 | 4.3 | | | | | | |
| Neutral oil | 77.5 | 15.8 | .87 | 1.39 | .19 | 0 | 0 | 100 |

of decomposition. The 1,700° F. oil, because of its small sample size, was distilled directly without preliminary separation into wide-boiling cuts. The atmospheric distillation of the first fraction from each of the two lower temperature oils and of the total 1,700° F. oil was made in a vacuum-jacketed, heligrid-packed column having a 5-ft. packed section. Fractions from these distillations contained about 10 ml. each, as this was the minimum quantity necessary for the desired analytical determinations.

Two types of columns were used for distillation of higher boiling compounds of the oils. Fraction 2 from the 1,200° F. oil and the residue from atmospheric distillation of the 1,700° F. oil were distilled in a 1-in. column containing a 6-ft. Stedman screen packing. Distillation of the former was conducted at 40 mm. pressure, so the pot temperature remained below 250° C., whereas the latter was distilled at a pressure of about 25 mm. of mercury. The 1,700° F. oil contained considerable quantities of naphthalene, so that special attention was necessary to keep this material from solidifying and plugging the takeoff system. Fraction 2 from the 1,500° F. oil was distilled in a spinning-band column having the following dimensions: Height, 600 mm.; diameter, 6 mm. The small-diameter tubes in this column plug easily; therefore, most of the naphthalene in the sample was removed before distillation. The sample was dissolved in about 4 volumes of pentane, cooled to minus 40° C., and filtered. After removal of the pentane, the oil was distilled at three successively reduced pressures as follows: About 30 pct. distillate was collected at 300 mm., 20 pct. at 100 mm., and 20 pct. at 50 mm. The stepwise reduction in pressure was used to avoid decomposition while operating at a high enough pressure to obtain good fractionation.

The fractions from the 1,200° F. oil were analyzed in a manner analogous to the N–T–U and Pumpherston naphthas. Many of the fractions from the two higher temperature oils were composed almost entirely of aromatics so that compositions were estimated from spectral and boiling-range data. Results for the three oils are shown in table 45.

## NONHYDROCARBON COMPOUNDS

The pH of the alkaline solution from extraction of the second fractions of the 1,200° and, 1,500° F. oils was adjusted to about 8 to liberate the phenols while retaining the carboxylic acids in solution. Because of the small quantities of oil originally available, this treatment yielded only about 5 ml. of phenols from each oil for examination. Each of the samples was separated by distillation into four fractions, and infrared spectra were obtained on the fractions. After qualitative identifications, quantitative determinations were made on the compounds boiling below about 220° C. The results are given in table 46. The absence of 4-methylphenol was unexpected, so the spectra were reexamined, but no appreciable quantity of this compound could be detected. Although the fractions from which the phenols were extracted had approximately the same boiling range, the pronounced difference in distribution of individual compounds between the two samples is evident. About two-thirds of the material boils above the dimethylphenol range in the 1,200° F. oil, whereas phenol, 2-methylphenol, and 3-methylphenol make up about 75 pct. of the phenols from the 1,500° F. oil.

TABLE 45.—*Content of hydrocarbons boiling below about 220° C. in crude shale oils produced at high temperatures*

| Compound | Volume-percent in crude oil retorted at | | |
|---|---|---|---|
| | 1,200° F. | 1,500° F. | 1,700° F. |
| Paraffins: | | | |
| Butanes | 0.04 | 0.01 | --------- |
| Pentanes | .16 | .05 | --------- |
| Hexanes | .28 | .02 | --------- |
| Heptanes | .65 | .05 | --------- |
| Octanes | .29 | .02 | --------- |
| Nonanes | .43 | --------- | --------- |
| Decanes | .90 | --------- | --------- |
| Undecanes | .17 | --------- | --------- |
| Dodecanes | .22 | --------- | --------- |
| Tridecanes | .25 | --------- | --------- |
| Total | 3.39 | .15 | --------- |
| Cycloparaffins: | | | |
| $C_5$ | .79 | .02 | --------- |
| $C_6$ | .26 | .05 | --------- |
| $C_7$ | 1.18 | .04 | --------- |
| $C_8$ | .58 | .05 | --------- |
| $C_9$ | .04 | .02 | --------- |
| $C_{10}$ | .02 | --------- | --------- |
| $C_{11}$ | .02 | --------- | --------- |
| $C_{12}$ | .03 | --------- | --------- |
| $C_{13}$ | .02 | --------- | --------- |
| Total | 2.94 | .18 | --------- |
| Aliphatic olefins: | | | |
| Butenes | .42 | --------- | --------- |
| Pentenes | 1.59 | .03 | --------- |
| Hexenes | .14 | .03 | --------- |
| Heptenes | .37 | .01 | --------- |
| Octenes | 1.49 | .10 | --------- |
| Nonenes | 1.07 | .03 | --------- |
| Decenes | .67 | --------- | --------- |
| Undecenes | .32 | --------- | --------- |
| Dodecenes | .38 | --------- | --------- |
| Total | 6.45 | .20 | --------- |
| Diolefins: | | | |
| Butadienes | .25 | --------- | --------- |
| Cyclopentadiene | .39 | --------- | --------- |
| Total | .64 | --------- | --------- |
| Cycloolefins: | | | |
| $C_5$ | 1.95 | --------- | --------- |
| $C_6$ | .61 | --------- | 0.01 |
| $C_7$ | .68 | .03 | --------- |
| $C_8$ | .37 | .10 | --------- |
| $C_9$ | .58 | .04 | --------- |
| $C_{10}$ | .22 | --------- | --------- |
| $C_{11}$ | .10 | --------- | --------- |
| $C_{12}$ | .23 | --------- | --------- |
| Total | 4.74 | .17 | .01 |
| Aromatics: | | | |
| Benzene | 4.88 | 15.50 | 22.56 |
| Toluene | 4.41 | 7.26 | .97 |
| Ethylbenzene | 2.11 | .38 | .19 |
| Xylenes | | 2.15 | |
| $C_9$-benzenes | 1.09 | .66 | .02 |
| $C_{10}$-benzenes | .19 | .72 | .02 |
| $C_{11}$-benzenes | .67 | .80 | .01 |
| Styrene | .52 | .69 | .04 |
| α- and β-Methylstyrene | .11 | .39 | --------- |
| $C_{10}$-styrenes | --------- | .10 | --------- |
| Indene | .80 | 1.16 | .07 |
| Naphthalene | .47 | 3.60 | 8.69 |
| Total | 15.25 | 33.41 | 32.57 |
| Grand total | 33.41 | 34.11 | 32.58 |

TABLE 46.—*Composition of phenols extracted from 1,200° and 1,500° F. oils, in volume-percent*

| Compound | 1,200° F. oil | 1,500° F. oil |
|---|---|---|
| Phenol | 1 | 35 |
| 2-Methylphenol | 3 | 22 |
| 3-Methylphenol | 3 | 19 |
| 2-Ethylphenol | 1 | 2 |
| 2,3-Dimethylphenol | 3 | 3 |
| 2,4-Dimethylphenol | 15 | 11 |
| 2,5-Dimethylphenol | --------- | 3 |
| 3,4-Dimethylphenol | 2 | --------- |
| 3,5-Dimethylphenol | 4 | --------- |
| Higher boiling material | 68 | 5 |

The tar bases were liberated and recovered only from the aqueous acid used to extract the 1,500° F. oil. The bases were separated by distillation into narrow-boiling fractions, and infrared spectra were obtained on the fractions. The compounds qualitatively identified were 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, 2,4,-dimethylpyridine, and 2,4,6-trimethylpyridine. As in shale oils from ordinary retorting methods, the 2,4,6-trimethylpyridine was the predominant compound. The 2,4-dimethylpyridine was present in significant amounts. Several pyridine homologs, whose infrared spectra were available for comparison, could not be detected. These were 2,3-dimethylpyridine, 2,6-dimethylpyridine, 3,4,-dimethylpyridine, 2-methyl-4-ethylpyridine, and 2-methyl-6-ethylpyridine.

## THERMALLY CRACKED N-T-U NAPHTHAS

Several naphthas resulting from thermal cracking of N-T-U shale oil were analyzed for tar acids, tar bases, sulfur, nitrogen, and hydrocarbon groups. The results, which are shown in table 47, indicate that the first four naphthas were similar to the primary naphthas described previously. This similarity seems reasonable, as shale oil itself is a pyrolytic product and these four naphthas were produced by single-pass thermal cracking of shale oil under various conditions. The fifth sample shown in the table was largely the result of recycle cracking and differed considerably in composition from the others, particularly in the quantity of saturates and

TABLE 47.—*Analyses of thermally cracked N-T-U naphthas*

| Naphtha No. | Tar acids vol.-pct. | Tar bases, vol.-pct. | Neutral naphtha vol.-pct. | | | Sulfur, wt.-pct. | Nitrogen, wt.-pct. |
|---|---|---|---|---|---|---|---|
| | | | Saturates | Olefins | Aromatics | | |
| 1 | 1.5 | 8.1 | 28 | 56 | 16 | 0.57 | 0.90 |
| 2 | 1.6 | 6.7 | 36 | 49 | 15 | .96 | 1.05 |
| 3 | 1.8 | 6.1 | 27 | 59 | 14 | 1.04 | .99 |
| 4 | 1.6 | 6.5 | 30 | 55 | 15 | .78 | .90 |
| 5 | 1.4 | 5.0 | 55 | 25 | 20 | .67 | 1.04 |

olefins present. Because of the difference in composition, a more detailed examination was made of this naphtha. It was produced at a temperature of 850° F., a pressure of 300 p.s.i.g., and a residence time of 26.3 min. The sample consisted of a mixture of about 3 parts second-pass product and 1 part first-pass product. The gravity and distillation range of the naphtha are given in table 48.

Tar acids and tar bases were extracted from the naphtha, leaving a neutral oil. Approximately 16 l. of naphtha was divided for treatment into four batches. Each batch was extracted first with 10 pct. sodium hydroxide, and then with 10 pct. sulfuric acid, and finally was neutralized with dilute sodium hydroxide and washed with water. Phenols were liberated from the sodium hydroxide solution by exhaustive treatment with carbon dioxide. Carboxylic acids were subsequently liberated from this solution by reducing the pH to about 2 with mineral acid. Tar bases were obtained from the sulfuric acid solution by neutralization with sodium hydroxide. Between each of these steps the aqueous phase was extracted with ether and the extracted material added to the appropriate organic phase. The combined quantities of products recovered from the batch treatments are shown in table 49 on a no-loss basis.

Table 48.—*Properties of a thermally cracked N–T–U naphtha*

| | |
|---|---|
| Specific gravity, 15.6°/15.6° C. | 0. 7920 |
| Gravity °API | 47. 2 |
| ASTM distillation at 760 mm.: | |
| Initial boiling point °C | 132 |
| 10 percent °C | 144 |
| 50 percent °C | 175 |
| 90 percent °C | 206 |
| End point °C | 225 |
| Sulfur weight-percent | 0. 67 |
| Nitrogen do | 1. 04 |

Table 49.—*Yields of products from extraction of thermally cracked N–T–U naphtha*

| | Weight-percent | Volume-percent |
|---|---|---|
| Tar acids: | | |
| Phenols | 1. 1 | 0. 9 |
| Carboxylics | . 3 | . 3 |
| Tar bases | 6. 5 | 5. 6 |
| Neutral oil | 92. 1 | 93. 2 |

## HYDROCARBON COMPOUNDS

Approximately 4,000 ml. of the neutral oil was distilled into about 1 pct. fractions. The first 35 pct. of the distillate was obtained at atmospheric pressure (585 mm.). When the

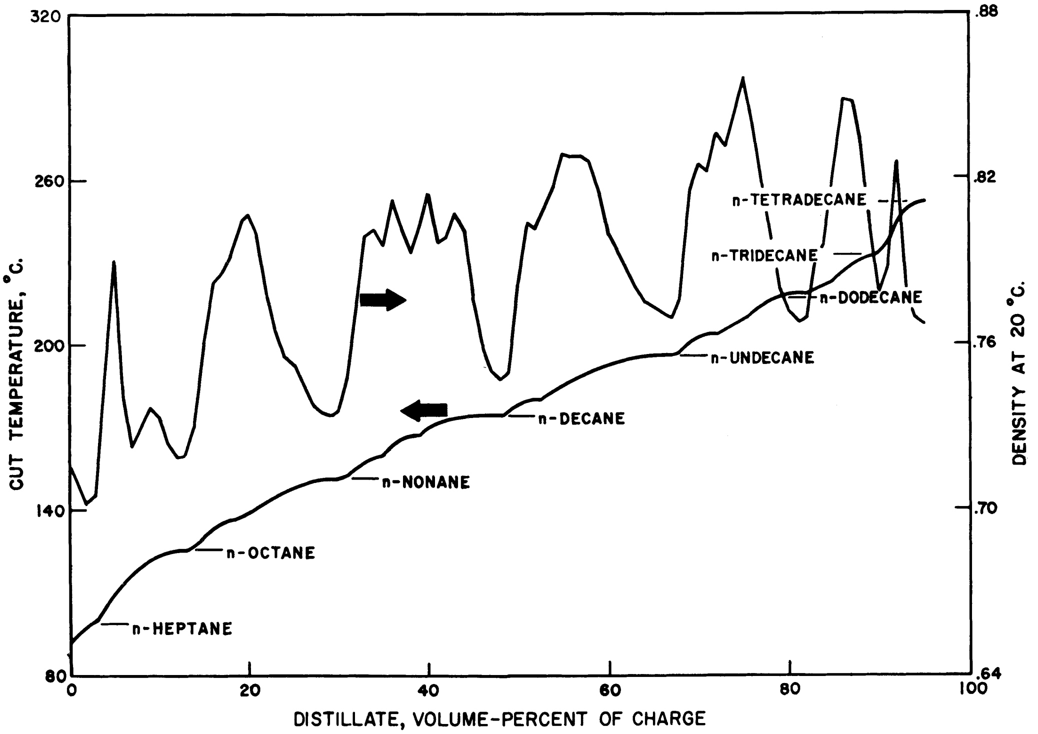

Figure 24.—Cut Temperature and Density of Each Fraction From Distillation of Thermally Cracked N–T–U Naphtha.

temperature in the distillation flask reached 185° C., the pressure was reduced to 80 mm., and the distillation was completed at this pressure. About 400 ml. of n-tetradecane was used as a pusher. The distillation curve (corrected to 760 mm.) and density of the fractions are shown in figure 24. The rather large quantity of normal paraffins in the sample is evident from the plateaus in the distillation curve, which generally correspond closely, as indicated, to the boiling points of the normal paraffins. The plateaus also correspond approximately to minima in the density curve.

The hydrocarbon-group composition of each fraction was determined by a silica-gel-adsorption analysis. From these data the volume of each hydrocarbon group distilled per degree rise in temperature was calculated, as has been described previously, with the results shown in figure 25. Again the large quantities of normal paraffins are evident. Also, from n-octane through n-dodecane the quantities of the individual compounds are about equal, showing the even distribution in this boiling range. When possible, the quantities of individual compounds were estimated. The predominant aromatic compound in each of the first 55 fractions was determined from ultraviolet absorption curves, as described for the primary N-T-U naphtha. When it was not possible to determine individual compounds, the amounts of molecular-weight groups were estimated. The results are given in table 50.

TABLE 50.—*Hydrocarbons in thermally cracked N-T-U naphtha*

| | Volume-percent |
|---|---|
| Paraffins: | |
| n-Heptane | 0.89 |
| Branched heptanes | .78 |
| n-Octane | 3.48 |
| Branched octanes | 2.80 |
| n-Nonane | 4.54 |
| Branched nonanes | 2.68 |
| n-Decane | 4.20 |
| Branched decanes | 2.52 |
| n-Undecane | 5.62 |
| Branched undecanes | 2.55 |
| n-Dodecane | 4.89 |
| Branched dodecanes | 2.07 |
| n-Tridecane | 2.12 |
| Branched tridecanes | 1.03 |
| Tetradecanes | .45 |
| Total | 40.62 |
| Cycloparaffins: | |
| $C_7$ | .54 |
| $C_8$ | 1.71 |
| $C_9$ | 3.02 |
| $C_{10}$ | 3.74 |
| $C_{11}$ | 2.66 |
| $C_{12}$ | 1.99 |
| $C_{13}$ | 1.41 |
| Total | 15.07 |
| Aliphatic olefins: | |
| n-Heptenes | .43 |
| Branched heptenes | .55 |
| n-Octenes | 1.75 |
| Branched octenes | 1.20 |
| n-Nonenes | 2.28 |
| Branched nonenes | 1.31 |
| n-Decenes | 1.43 |
| Branched decenes | 1.25 |
| n-Undecenes | 2.06 |
| Branched undecenes | .91 |
| n-Dodecenes | .56 |
| Branched dodecenes | .81 |
| n-Tridecenes | .54 |
| Branched tridecenes | .87 |
| Tetradecenes | .25 |
| Total | 16.20 |
| Cycloolefins: | |
| $C_7$ | .93 |
| $C_8$ | 1.44 |
| $C_9$ | 2.41 |
| $C_{10}$ | 1.89 |
| $C_{11}$ | 1.00 |
| $C_{12}$ | 1.20 |
| $C_{13}$ | .64 |
| Total | 9.51 |
| Aromatics: | |
| Benzene | .02 |
| Toluene | .38 |
| Ethylbenzene | .16 |
| p-Xylene | .32 |
| m-Xylene | .98 |
| o-Xylene | .43 |
| iso-Propylbenzene | .04 |
| n-Propylbenzene | .05 |
| 1-Methyl-4-ethylbenzene | .89 |
| 1-Methyl-3-ethylbenzene | .08 |
| 1-Methyl-2-ethylbenzene | .52 |
| 1,3,5-Trimethylbenzene | |
| 1,2,4-Trimethylbenzene [1] | .93 |
| iso-Butylbenzene | |
| sec-Butylbenzene | |
| tert-Butylbenzene | |
| 1,2,3-Trimethylbenzene | 1.46 |
| 1-Methyl-4-isopropylbenzene [1] | |
| 1-Methyl-3-isopropylbenzene | |
| 1-Methyl-2-isopropylbenzene | |
| 1,4-Diethylbenzene | 1.18 |
| 1,3-Diethylbenzene | .20 |
| Other $C_{10}$-benzenes | 1.13 |
| $C_{11}$-benzenes | 4.10 |
| $C_{12}$-benzenes | 2.27 |
| $C_{13}$-benzenes | .76 |
| Total | 15.90 |
| Grand total | 97.30 |

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[1] Predominant compound in groups as indicated by ultraviolet-absorption data.

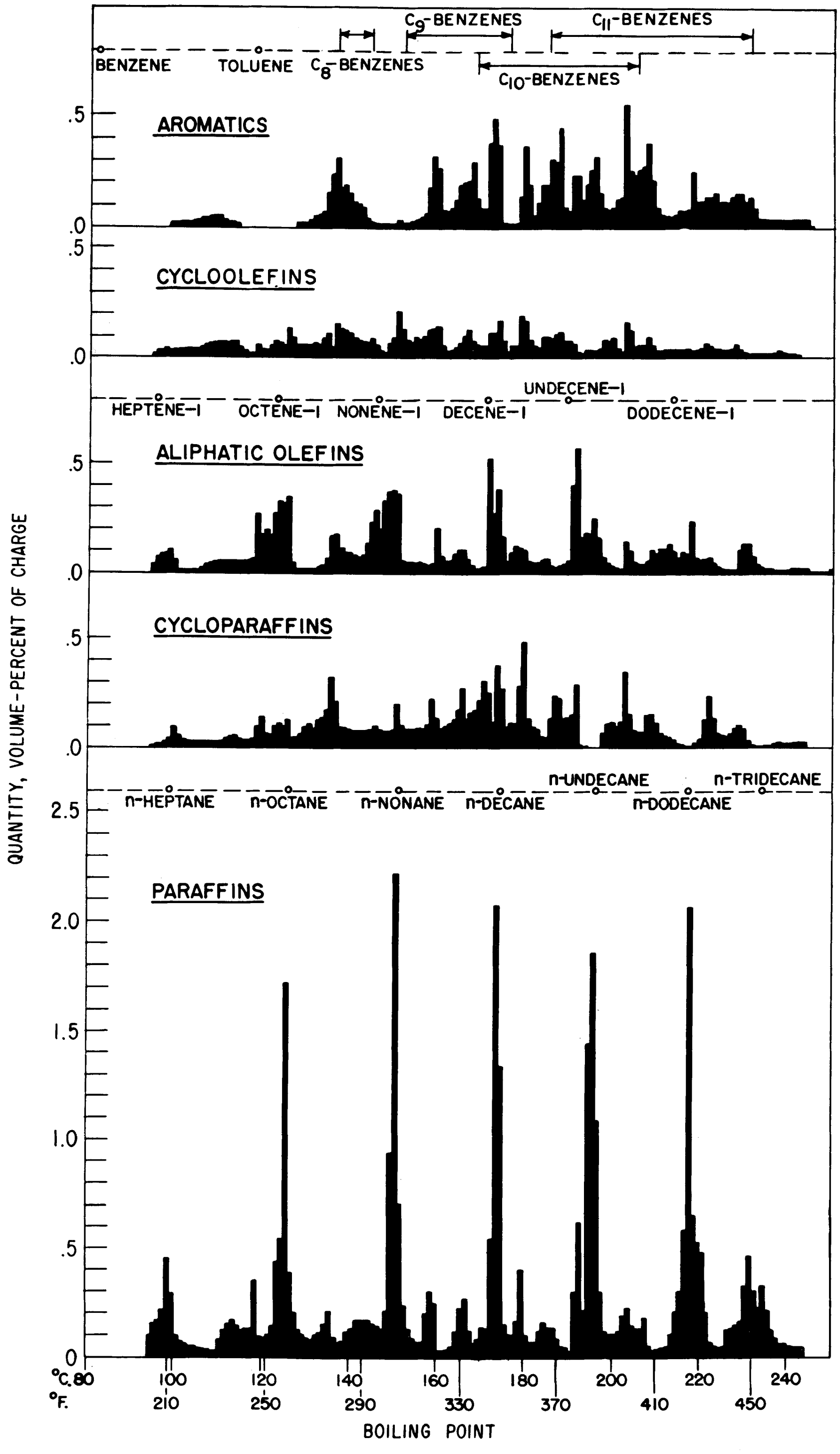

Figure 25.—Amounts of Various Classes of Hydrocarbons in Thermally Cracked N-T-U Naphtha.

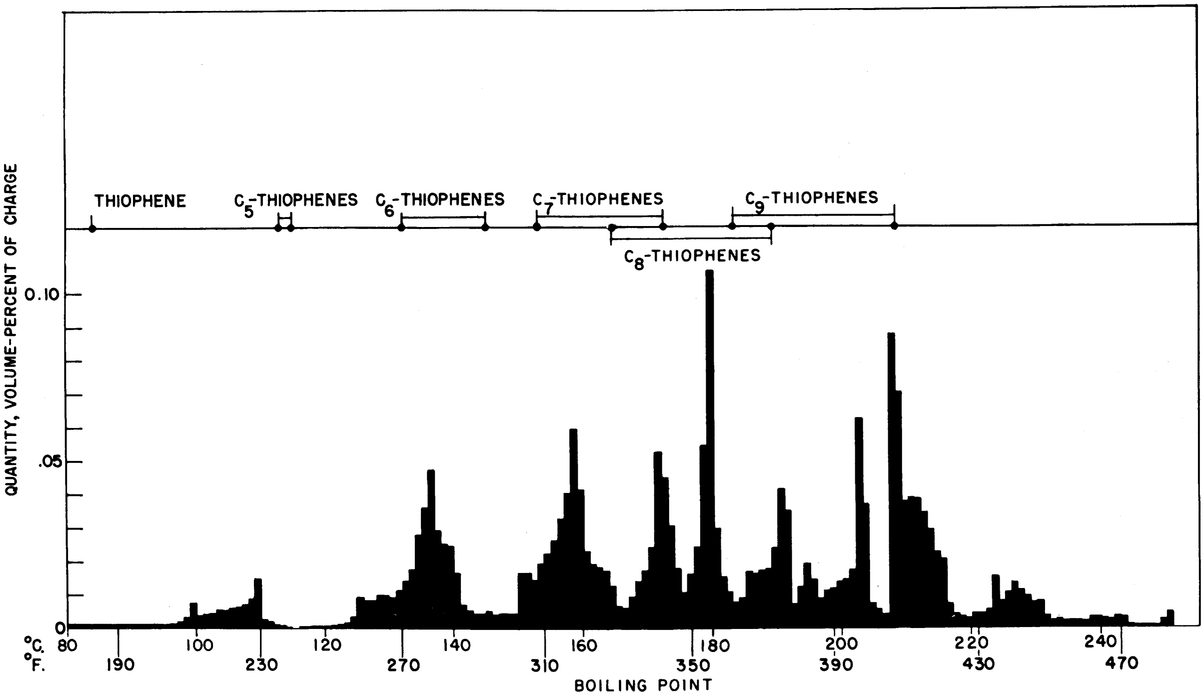

FIGURE 26.—Amounts of Sulfur Compounds in Thermally Cracked N-T-U Naphtha.

## NONHYDROCARBON COMPOUNDS

The nonhydrocarbon compounds occur in the tar acids, tar bases, and neutral oil. The distribution of the sulfur compounds in the neutral oil is plotted in figure 26 in the same manner that has been described previously.

Approximately 125 ml. of phenols, recovered from the aqueous sodium hydroxide by the method described previously, was charged to a small packed fractionating column. A total of 85 fractions of about 1 ml. each was obtained. From infrared spectra on the fractions qualitative identifications were made. Quantitative determinations of individual components were made on all fractions boiling below about 220° C. The results are given in table 51. Quantitative results were obtainable on only about the first 40 pct. of the distillate, as calibrating patterns were not available for all of the compounds present in the remainder of the fractions. The values given in table 51 for some of the compounds represent only part of the total amount in the naphtha, as these compounds were also present in some of the fractions having interfering substances. The principal differences in composition between these phenols and those from the primary naphtha are the much smaller quantity of 4-methylphenol and the much larger quantity of 2,4-dimethylphenol in the phenols from the cracked naphtha.

TABLE 51.—*Composition of the phenols from thermally cracked N-T-U naphtha, in volume-percent*

| Compound | Phenols | Naphtha |
|---|---|---|
| Phenol | 2.3 | 0.02 |
| 2-Methylphenol | 6.7 | .06 |
| 3-Methylphenol | 3.9 | .04 |
| 4-Methylphenol | 2.9 | .03 |
| 2-Ethylphenol | 1.1 | .01 |
| 3-Ethylphenol | .1 | .001 |
| 2,3-Dimethylphenol | 1.6 | .01 |
| 2,4-Dimethylphenol | 13.2 | .12 |
| 2,5-Dimethylphenol | 4.2 | .04 |
| 2,6-Dimethylphenol | 3.2 | .03 |
| 3,5-Dimethylphenol | .6 | .01 |
| Higher boiling phenols | 60.2 | .54 |

Using the same distillation equipment as for the tar acids, a sample of about 350 ml. of tar bases was distilled to give 236 overhead fractions of about 1 ml. volume each. Ultraviolet and infrared spectra on the first 35 of these fractions showed the presence of 2-methylpyridine, 2,4-dimethylpyridine, and 2,4,6-trimethylpyridine. The remaining fractions were not examined, as reference spectra for higher boiling pyridines were not available at the time this work was done.

## NAPHTHAS CHARACTERIZED IN METHOD FOR ANALYSIS OF CRUDE SHALE OIL

Crude shale oils from numerous sources have been analyzed by the Bureau of Mines method.[76][77] This method consists essentially of dis-

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[76] Stevens, R. F., Dinneen, G. U., and Ball, J. S., Analysis of Crude Shale Oil: Bureau of Mines Rept. of Investigations 4898, 1952, 20 pp.

[77] Albright, C. S., Van Meter, R. A., Dinneen, G. U., and Ball, J. S., Analysis of Crude Shale Oil. 2. Some Brazilian and U.S.A. Oils: Bureau of Mines Rept. of Investigations 5286, 1956, 28 pp.

tilling the oil into fractions taken at 25° C. intervals and making certain determinations on the fractions. One part of the method consists of compositing fractions to give a naphtha having a boiling range approximately equivalent to that of the naphthas discussed previously. The composite is analyzed for tar acids, tar bases, hydrocarbon groups, sulfur, and nitrogen. The results of such analyses on oils from Colorado shale and from several foreign countries are shown in table 52. As the data in table 52 were all obtained by the same method, they are useful for direct comparison of the various materials. However, they cannot be used to predict the properties of commercial products that may be made from the crude oils.

## COMMERCIAL PRODUCTS FROM FOREIGN SOURCES

Bureau of Mines personnel have made visits to several foreign countries [78–81] to observe oil-shale operations, and during these visits they secured samples of commercial products. Analyses of these products, many of which are finished motor fuels, are given in tables 53 and 54.

TABLE 52.—*Properties of naphthas analyzed in method for analysis of crude shale oil*

| Source and retort | Naphtha in crude oil vol.-pct. | Tar acids, vol.-pct. | Tar bases, vol.-pct. | Composition of neutral naphtha, vol.-pct. | | | Sulfur, wt.-pct. | Nitrogen, wt.-pct. |
|---|---|---|---|---|---|---|---|---|
| | | | | Saturates | Olefins | Aromatics | | |
| U.S.A. (Colorado): | | | | | | | | |
| Gas combustion | 4.4 | 4.4 | 7.5 | 27 | 51 | 22 | 1.03 | 1.17 |
| Gas flow | 1.5 | 2.6 | 8.2 | 27 | 42 | 31 | .71 | 1.30 |
| Parry | 14.9 | 1.2 | 4.8 | 27 | 48 | 25 | .89 | .51 |
| Fischer assay | 13.7 | 3.5 | 5.0 | 33 | 56 | 11 | ------------ | .74 |
| U.S.A. (Tennessee): | | | | | | | | |
| Royster-TVA | 6.0 | 3.2 | 1.6 | 25 | 21 | 54 | 2.34 | .22 |
| Spain: | | | | | | | | |
| Pumpherston type | 13.8 | 1.7 | 1.0 | 42 | 42 | 16 | .27 | .18 |
| South Africa: | | | | | | | | |
| Salermo | 19.1 | 1.8 | .6 | 37 | 48 | 15 | .43 | .14 |
| Australia: | | | | | | | | |
| Pumpherston | 14.6 | 1.4 | 2.3 | 45 | 43 | 12 | .41 | .10 |
| Sweden: | | | | | | | | |
| Rochesholm | 16.5 | 2.2 | .7 | 24 | 35 | 41 | 1.42 | .17 |
| Ljungstrom | 76.8 | .4 | .2 | 63 | 11 | 26 | .70 | .07 |
| Scotland: | | | | | | | | |
| Pumpherston | 19.5 | 1.2 | .8 | 47 | 43 | 10 | .27 | .13 |
| France: | | | | | | | | |
| Pumpherston | 2.3 | ------------ | ------------ | ------------ | ------------ | ------------ | .42 | .40 |
| Marecaux | 23.5 | 1.6 | .4 | 31 | 41 | 28 | 3.17 | .15 |
| Cantieny | 27.9 | 1.2 | 1.2 | 25 | 22 | 53 | 2.94 | .16 |
| Lantz | 19.7 | 2.0 | 2.0 | 37 | 47 | 16 | .50 | .11 |
| Brazil (Paraiba Valley): | | | | | | | | |
| Fischer assay | 16.4 | 2.7 | 6.4 | 19 | 60 | 21 | ------------ | 1.17 |

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[78] Guthrie, Boyd and Klosky, Simon, The Oil-Shale Industries of Europe: Bureau of Mines Rept. of Investigations 4776, 1951, 73 pp.

[79] Kraemer, A. J., and Thorne, H. M., Oil Shale Operations in New South Wales, Australia: Bureau of Mines Rept. of Investigations 4796, 1951, 48 pp.

[80] Thorne, H. M., and Kraemer, A. J., Oil-Shale in Spain: Bureau of Mines Rept. of Investigations 4736, 1950, 21 pp.

[81] ———, Oil-Shale Operations in the Union of South Africa, October 1947: Bureau of Mines Rept. of Investigations 5019, 1954, 31 pp.

TABLE 53.—*Analyses of products from foreign oil-shale operations, in volume-percent*

| Description of sample | Tar acids | Tar bases | Composition of neutral distillate | | |
|---|---|---|---|---|---|
| | | | Saturates | Olefins | Aromatics |
| Light gasoline (Sweden) | (1) | (1) | 47 | 42 | 11 |
| Crude gasoline (Sweden) | 0.9 | 0.9 | 28 | 35 | 37 |
| Motor gasoline (Sweden) | .5 | .5 | 50 | 33 | 17 |
| Crude gasoline (Pumpherston, France) | .4 | 1.6 | 42 | 42 | 16 |
| Motor fuel (Pumpherston, France) | .7 | 2.1 | 44 | 40 | 16 |
| Gasoline (Lantz, France) | .2 | .0 | 38 | 43 | 19 |
| Motor fuel (Scotland) | .4 | .3 | 50 | 43 | 7 |
| Scrubber naphtha (Australia) | .5 | .6 | 42 | 51 | 7 |
| Pressure distillate (Australia) | 1.3 | 1.0 | 43 | 46 | 11 |
| Acid-treated heavy naphtha (Australia) | .3 | .4 | 43 | 40 | 17 |
| Caustic-treated light naphtha (Australia) | .5 | .5 | 44 | 52 | 4 |
| Motor fuel (Australia) | .6 | .3 | 38 | 47 | 15 |
| Gasoline (Spain) | .8 | .9 | 42 | 44 | 14 |
| Pressure distillate (South Africa) | 2.9 | [2] 2.9 | 46 | 38 | 16 |
| Motor fuel (South Africa) | .4 | .6 | 49 | 40 | 11 |

[1] Sample too volatile for accurate analysis.
[2] Part of this high result is probably due to polymer formation.

TABLE 54.—*Nitrogen and sulfur analyses on products from foreign oil-shale operations*

| Description of sample | Nitrogen, wt.-pct. | Type-sulfur analyses expressed as weight-percent sulfur in each type | | | | | |
|---|---|---|---|---|---|---|---|
| | | Total | Elemental | Thiol | Sulfide | Disulfide | Residual |
| Light gasoline (Sweden) | 0.00 | 1.46 | 0.00 | 0.40 | 0.32 | 0.03 | 0.71 |
| Crude gasoline (Sweden) | .10 | 1.45 | .00 | .19 | .24 | .01 | 1.01 |
| Motor gasoline (Sweden) | .00 | .25 | .00 | .04 | .00 | .02 | .19 |
| Crude gasoline (Pumpherston, France) | .14 | .35 | .00 | .06 | .00 | .00 | .29 |
| Motor fuel (Pumpherston, France) | .00 | .27 | .00 | .00 | .00 | .00 | .27 |
| Gasoline (Lantz, France) | .00 | .20 | .00 | .04 | .00 | .00 | .16 |
| Motor fuel (Scotland) | .01 | .10 | .00 | .00 | .00 | .00 | .10 |
| Scrubber naphtha (Australia) | .01 | .20 | .00 | .00 | .00 | .00 | .20 |
| Pressure distillate (Australia) | .05 | .23 | .00 | .01 | .00 | .00 | .22 |
| Acid-treated heavy naphtha (Australia) | .00 | .31 | .00 | .00 | .00 | .00 | .31 |
| Caustic-treated light naphtha (Australia) | .00 | .11 | .00 | .01 | .00 | .00 | .10 |
| Motor fuel (Australia) | .00 | .23 | .00 | .06 | .00 | .01 | .16 |
| Gasoline (Spain) | .09 | .39 | .00 | .05 | .05 | .01 | .28 |
| Pressure distillate (South Africa) | .24 | .38 | .00 | .00 | .00 | .00 | .38 |
| Motor fuel (South Africa) | .00 | .36 | .00 | .03 | .00 | .01 | .32 |

# PROCEDURE FOR ANALYSIS OF SHALE-OIL NAPHTHAS

Shale-oil naphtha consists primarily of hydrocarbons with smaller amounts of sulfur-, nitrogen-, or oxygen-containing compounds. The characterization of such material may be undertaken in a number of ways. The general approach selected to obtain the results reported in this paper was to separate groups of compounds having similar properties. Each of these groups was subjected to detailed examination using such techniques as distillation, adsorption, spectroscopy, and derivative formation.

## GROUP SEPARATIONS

An outline showing the five groups of compounds separated from the raw naphtha is given in figure 27. The acidic constituents were removed first by successive extractions (usually three) with 10 pct. aqueous sodium hydroxide. Aqueous reagent equivalent to 50 pct. by volume of the naphtha was used for each of the extractions. The tar-acid-free naphtha was divided into two portions—a major one for the extraction of basic constituents and a smaller one for preparation of a pyrrole concentrate. The basic constituents were removed by successive extractions (usually three) with 10 pct. aqueous sulfuric acid. The extracts obtained were saved for later analyses. The neutral oil was washed with dilute caustic, about 2 pct., and finally with distilled water. The neutral oil was stored in an inert atmosphere in dark bottles under refrigeration in order to minimize discoloration and gum formation.

Numerous variations are possible in the strengths of reagents and in the order of their application for the extraction of acidic and basic constituents from organic materials. Some of the more usual ones were investigated before the procedure described in the preceding paragraph was selected. Equal quantities were extracted with 5, 10, or 20 pct. reagents, but, in general, formation of troublesome emulsions and insoluble polymers was less with 10 pct. reagents. The number of extractions required to produce constant volume of raffinate varied. In most instances, three were sufficient, but when large volumes of naphtha were being treated, more extractions were sometimes necessary. Alternate extractions with aqueous base and acid were tried in an effort to increase the amount of material extracted. No greater extraction was attained, and difficulties caused by fluctuations in raffinate volume were introduced. The raffinates frequently appeared to gain volume when extracted with acid and then to lose this gained volume and more on subsequent extraction with base. The order in which the reagents were applied was selected because difficulties caused by the formation of an insoluble third phase were distinctly less when aqueous base was used first.

The pH of the aqueous base used to extract tar acids was lowered to about 8.5 by the ad-

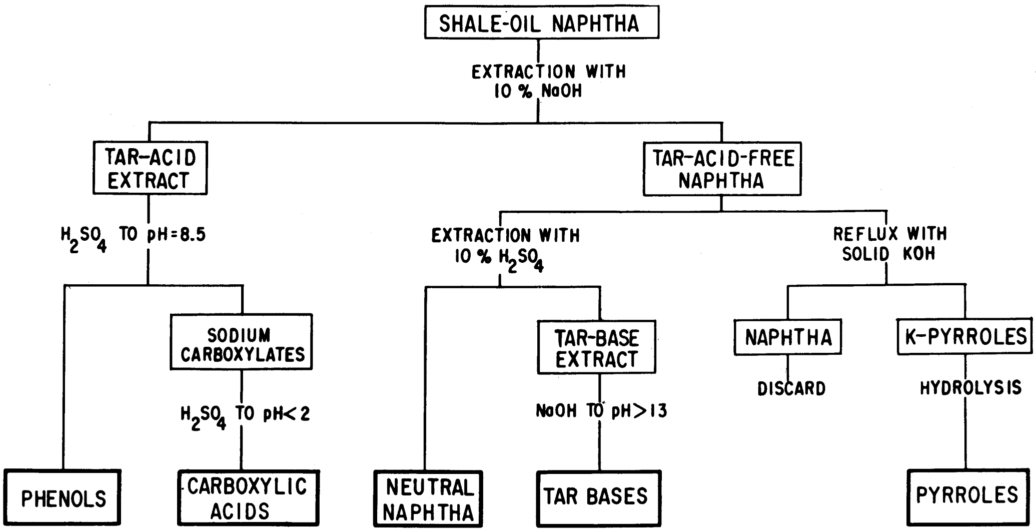

FIGURE 27.—Separation of Groups of Compounds From Shale-Oil Naphtha.

dition of carbon dioxide or mineral acid. This procedure liberated most of the phenols while retaining the carboxylic acids in solution as the sodium salts. The liberated phenols were extracted from the aqueous solution with ether. The pH of the solution was then reduced below 2 to free the carboxylic acids, which were also extracted with ether.

The pH of the aqueous acid used to extract tar bases was raised to about 13 with aqueous sodium hydroxide in order to liberate the organic bases. These consisted principally of pyridines with smaller amounts of pyrroles that were sufficiently basic to be extracted with the aqueous reagent.

Reactive pyrroles were removed from a portion of the tar-acid-free naphtha by reaction with solid potassium hydroxide. The reaction was carried out at the reflux temperature of the naphtha, and water formed in the reaction was removed from the reflux stream by a side-arm-type trap. Progress of the reaction was judged by the rate of water formation. After completion of the reaction, the naphtha was decanted from the caustic cake, which was washed free of residual naphtha with volative solvents. The caustic was then hydrolyzed to regenerate the original pyrroles.

## DETAILED EXAMINATIONS

A complete analysis would require the quantitative determination of every component in the sample. This was impractical, so the procedure adopted was a compromise based in each case on the amount of time and manpower available for the study.

### NEUTRAL OIL

The neutral oil contained the hydrocarbons and most of the sulfur compounds originally present in the naphtha, as well as some nitrogen and oxygen compounds that were not removed by extraction. The principal analytical effort was placed on the first two groups of compounds, with identifications in the latter groups being incidental.

#### HYDROCARBON COMPOUNDS

A portion, usually 4 l., of the neutral oil was distilled in an efficient fractionating column into 0.5- to 1.0-pct. fractions. The distillation was started at atmospheric pressure, and several successively lower pressures were used to keep the temperature in the distillation flask below about 175° C., thus reducing the probability of decomposition. A record of cut temperatures of the fractions and corresponding barometric pressures was maintained so that a curve of distillation temperatures equivalent to those at a pressure of 760 mm. of mercury could be plotted.

Density and refractive index were measured on each of the distillation fractions. These properties in conjunction with the distillation curve indicated that certain fractions were sufficiently similar so that they could be combined to reduce the subsequent analytical work without appreciably reducing the information obtained.

The quantities of paraffins, cycloparaffins, aliphatic olefins, cyclic olefins, and aromatics in each of the combined fractions from the preceding screening operation were estimated from a silica-gel-adsorption analysis on the fraction. This analytical procedure is described in the following section of this report. From the data obtained, a plot was prepared for each group of hydrocarbons showing the quantity distilled per degree rise in temperature. This method of plotting the data yielded a curve with peaks corresponding to single compounds or groups of compounds of similar boiling points. The quantities of these were estimated from the areas under appropriately chosen portions of the curves. Ultraviolet spectra of the fractions were used to aid in identifying the individual aromatic hydrocarbons responsible for peaks in the aromatic curve.

#### SULFUR COMPOUNDS

A group-sulfur analysis was run on the neutral oil to provide an estimate of the content of free sulfur, hydrogen sulfide, thiols, sulfides, disulfides, and residual sulfur. Unfortunately the large quantities of unsaturates in shale-oil naphthas make estimation of these types of compounds difficult and cause uncertainties in the results obtained. Even though the results are only approximate, they do indicate the predominant type of sulfur in the naphtha.

The weight-percent of sulfur was determined on the fractions from distillation of the neutral naphtha and was used to plot a curve showing the quantity sulfur compounds distilled per degree temperature rise. The location of the peaks in this curve also gave some indication as to the predominant type of sulfur compounds in the naphtha.

Results by the two preceding techniques suggested that thiophenes are the predominant sulfur compounds in shale-oil naphthas. A systematic scheme for the isolation and identification of individual compounds of this type is described in the following section of this report.

The nonthiophenic sulfur in shale-oil naphthas consists mostly of sulfides and disulfides. A systematic procedure for isolating and identifying individual compounds of these types has not been established; thus investigation of any given naphtha must be designed to yield the specific information desired.

## EXTRACTS

With the exception of the neutral oil, the group separations shown in figure 27 yielded concentrates that consisted predominantly of one class of compounds. Hence, the general analytical approach for these groups—phenols, carboxylic acids, tar bases, and pyrroles—was similar. In each instance the material was distilled to yield fractions each of which contained only a relatively few components. An attempt was made to identify and to determine quantitatively individual compounds by use of spectroscopy, chromatography, and derivative formation. Application of these techniques was frequently complicated by the fact that the group separations were not selective enough to eliminate all interfering substances. Therefore, treatment of the fractions to remove such substances was often necessary, but no generally applicable technique can be described.

# ANALYTICAL METHODS

Many of the procedures used in the experimental part of this paper are the accepted techniques of organic analytical chemistry. However, because of some unusual characteristics of shale-oil naphtha, it was necessary in certain instances to develop new methods, or to modify existing methods, in order to obtain the desired information. The four most important of these are described in this section. They are: Determination of hydrocarbon groups by silica-gel adsorption,[82] determination of nitrogen by the Kjeldahl method,[83] determination of basic nitrogen by perchloric acid titration,[84] and a systematic procedure for the identification of thiophene homologs.[85]

## HYDROCARBON GROUPS BY ADSORPTION

The method is a displacement-type adsorption in which the sample is passed into a column of silica gel that selectively adsorbs the compounds present, arranging them in groups having similar adsorbabilities. The sample is forced through the column by an appropriate desorbing liquid and collected in small fractions as it emerges. The refractive index of each fraction is determined and plotted against the volume sum of desorbed sample to give an adsorptogram, an example of which is shown in figure 28. The three plateaus on the curve consist of hydrocarbon groups as indicated in the figure. From the curve the percentage by volume of each of these groups may be calculated.

The following apparatus is employed:

Column as shown in figure 29.
Tip shown in figure 30 for collecting fractions of about 0.15 ml. each.
Refractometer capable of measuring refractive index to ± 0.001.

Reagents include:

Silica gel, Davison Chemical Corp., 28- to 40-mesh.
Silica gel, Davison Chemical Corp., code 922 or equivalent, through 200-mesh.
2-Propanol, 98 pct.
Compressed gas, nitrogen or helium.

**Procedure.**—The column is prepared for analysis by placing a few grains of coarse gel in the tip to support the finer material and to prevent clogging of the tip with fine material. Fifty grams of the finer gel is then added, and the column is tapped gently for several minutes with a rubber-covered rod to pack the gel uniformly. This will fill the column to about the level of the upper outlet on the water jacket. Cooling water passed through the jacket on the column is used to dissipate the heat of adsorption. The collection tip is clamped securely in a position such that it is level along line AB (fig. 30) and the end of the column touches the funnel portion of the tip some distance from the capillary opening. The tip is calibrated for the volume delivered in this position.

A 10-ml. sample is introduced into the reservoir by means of a pipet. The reservoir is closed, and a pressure of 2 p.s.i.g. is applied, using an inert gas, until all the sample has entered the silica gel. The pressure is carefully released, and the reservoir is washed down with a small amount of desorbent (2-propanol). When this has entered the adsorbent, a few grams of fresh gel is added to the reservoir to adsorb the desorbing liquid and prevent it from mixing with the sample. The reservoir is then filled with 2-propanol, and a pressure of 10 p.s.i.g. is applied for the remainder of the analysis. As the sample emerges from the column, fractions containing about 0.15 ml. each are collected in small test tubes, which are then stoppered to prevent evaporation.

The refractive index of each fraction is determined and plotted against the volume sum of the desorbed sample to give an adsorptogram. From this curve the percent by volume of each group of compounds is calculated. In this calculation the break between groups of compounds is assumed to occur between the fractions showing the greatest difference in refractive indices. If two differences are approximately equal, the break is taken at the midpoint of the fraction between these differences. The break at the end of the curve is assumed to represent a recovery of 100 pct. The volume-percent of a group of compounds is calculated by dividing the volume between adjacent breaks by the total volume of filtrate and multiplying by 100. Subdivisions within the groups are obtained by calculation.

The sulfur and nitrogen compounds remaining in a naphtha after extraction with aqueous

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[82] Dinneen, G. U., Bailey, C. W., Smith, J. R., and Ball, John S., Shale-Oil Naphthas, Analysis of Small Samples by the Silica Gel Adsorption Method: Anal. Chem., vol. 19, 1947, pp. 992–998.

[83] Lake, G. R., McCutchan, P., Van Meter, R., and Neel, J. C., Effects of Digestion Temperature of Kjeldahl Analyses: Anal. Chem., vol. 23, 1951, pp. 1634–1638.

[84] Moore, R. T., McCutchan, P., and Young, D. A., Basic Nitrogen Determination by Titration With Perchloric Acid: Anal. Chem., vol. 23, 1951, pp. 1639–1641.

[85] Kinney, I. W., Jr., and Cook, G. L., Identification of Thiophene and Benzene Homologs, Mass Spectral Correlations: Anal. Chem., vol. 24, 1952, pp. 1391–1396.

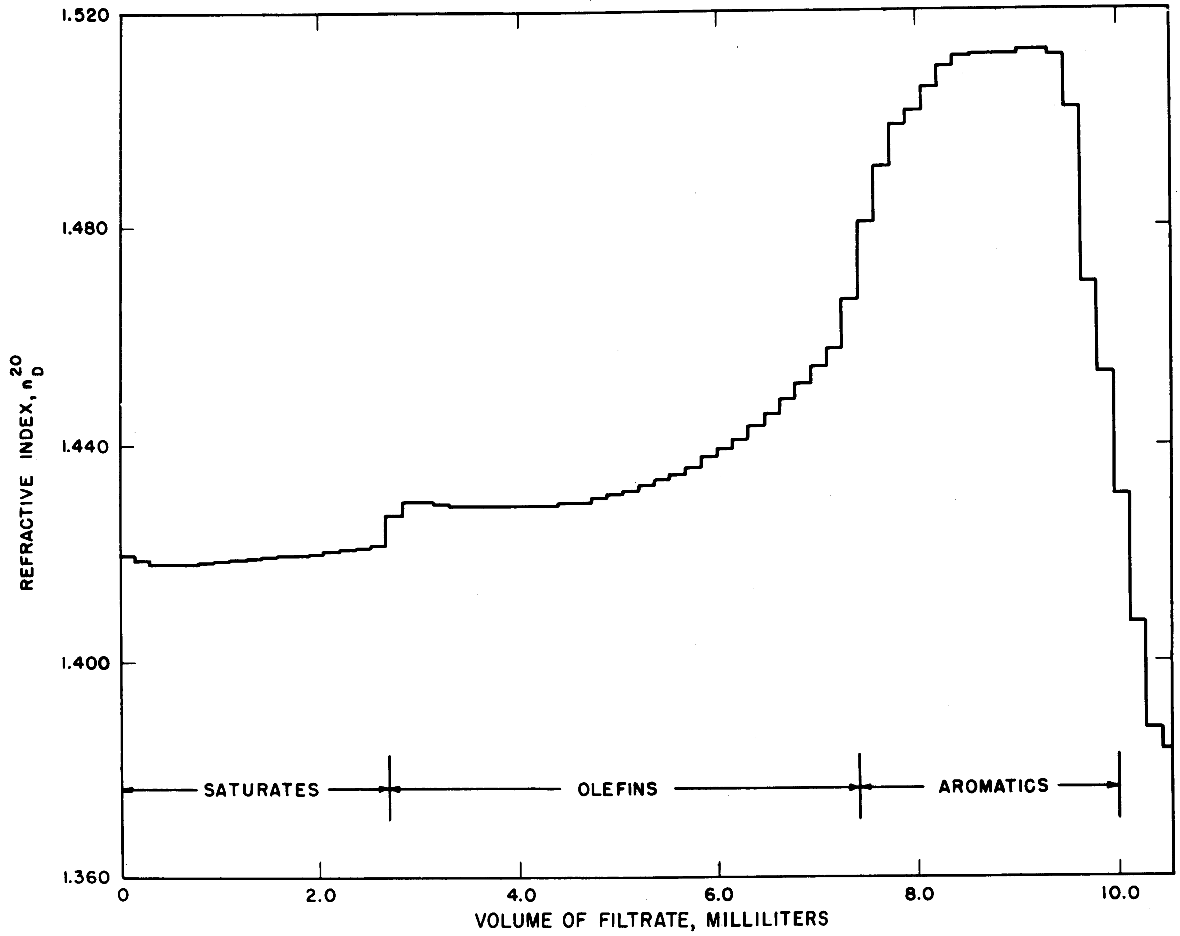

FIGURE 28.—Adsorptogram of a Shale-Oil Naphtha.

acid and base generally form part of the aromatic plateau on the adsorptogram. The percentage of sulfur compounds is calculated by the following equation and subtracted from the total percentage of aromatics:

$$V_s=\frac{P_sMD_f}{32D_s},$$

where $V_s$ is the volume-percent of sulfur compounds, $P_s$ is the weight-percent of sulfur, $M$ is the average molecular weight of the sulfur compounds in the boiling range of the fraction being analyzed, $D_f$ is the density of the fraction at 20° C., 32 is the atomic weight of sulfur, and $D_s$ is the average density of the sulfur compounds at 20° C. An approximation for this correction, which is usually sufficiently accurate, may be made by omitting the densities in the above equation. The correction for nitrogen compounds is made by a calculation analogous to that for sulfur compounds.

The saturates are further subdivided into aliphatic and cyclic compounds by a calculation[86] based on refractive index and boiling point. The following equations are used with the choice dependent on the mid-boiling point of the sample:

If $t$ is 190° C. or less

$$S_{cp}=\frac{S(N_s-0.000346t-1.354)}{0.039-0.000067t}.$$

If $t$ is greater than 190° C.

$$S_{cp}=\frac{S(N_s-0.000187t-1.384)}{0.000092t+0.009}.$$

In either case

$$S_p=S-S_{cp},$$

where

$S_{cp}$=percent of cycloparaffins in sample

$S_p$=percent of paraffins in sample

$S$=total percent of saturates in sample

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[86] Dinneen, G. U., Thompson, C. J., Smith, J. R., and Ball, John S., Adsorption Analysis by Displacement Techniques: Anal. Chem., vol. 22, 1950, pp. 871-876.

$N_s$=refractive index of midpoint of saturate plateau from adsorptogram

$t$=temperature in degrees centigrade of the 50 pct. evaporated point of an ASTM distillation [87] or the average boiling point of a narrow-boiling fraction.

The following similar set of equations is used for calculating the content of aliphatic and cyclic olefins in the sample:

If $t$ is 175° C. or less

$$U_{co}=\frac{U(N_u-0.000344t-1.370)}{0.061-0.000177t}.$$

If $t$ is greater than 175° C.

$$U_{co}=\frac{U(N_u-0.000185t-1.397)}{0.034-0.000017t}.$$

In either case

$$U_{ao}=U-U_{co}$$

where

$U_{co}$=percent of cyclic olefins in sample

$U_{ao}$=percent of aliphatic olefins in sample

$U$=total percent of olefins in sample

$N_u$=average refractive index of olefin plateau from adsorptogram. (This may usually be estimated with sufficient accuracy from visual inspection of the adsorptogram.)

$t$=temperature in degrees centigrade of the 50 pct. evaporated point of an ASTM distillation or the average boiling point of a narrow-boiling fraction.

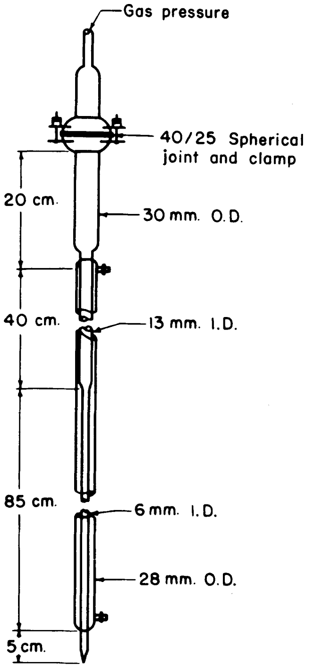

FIGURE 29.—Column for Hydrocarbon-Group Analysis.

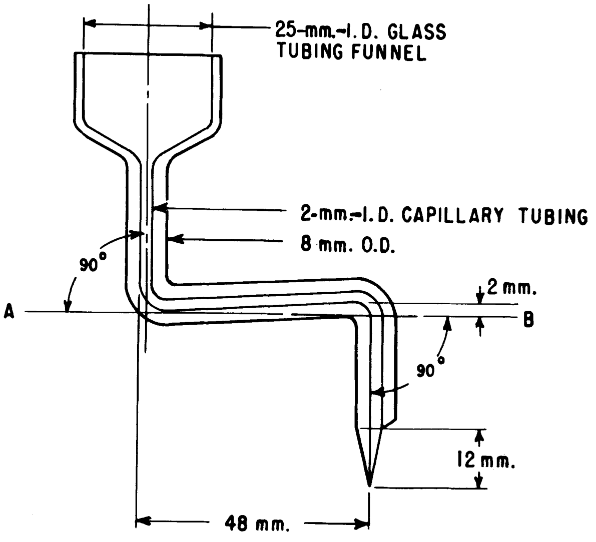

FIGURE 30.—Collection Tip Used in Hydrocarbon-Group-Analysis Method.

## DEVELOPMENT OF METHOD

An accurate determination of the constituent hydrocarbon groups is a fundamental requirement in the study of naphtha composition. However, the composition and properties of shale-oil naphtha limit the usefulness of many tests that are commonly applied to materials of this boiling range in the petroleum industry. Naphtha from shale oil contains large quantities of unsaturated hydrocarbons in addition to saturates and aromatics that are found in straight-run petroleum naphthas. Also, appreciable quantities of compounds that contain an atom of sulfur, nitrogen, or oxygen are present. Refractive index values are often difficult to obtain because of the color of the material. Furthermore, olefins interfere with methods of estimating aromatics from this property. Particularly in the United States, the bromine number has been used extensively in the analysis of petroleum fractions to indicate unsaturation. Many modifications of the procedure have been proposed in an effort to promote addition and minimize substitution reactions. However, application of several bromine-number procedures to shale-oil naphthas gave erratic and apparently anomalous results. These facts led to a search for other possible methods of determining hydrocarbon groups, particularly olefins. It appeared that selective adsorption offered the most promise, so an investigation of it was undertaken that resulted in the development of the method presented here.

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[87] American Society for Testing Materials, Standard Method of Test for Distillation of Gasoline, Naphtha, Kerosine, and Similar Petroleum Products (D86–56): 1958 Book of ASTM Standards, pt. 7, Philadelphia, Pa., 1958, pp. 8–15.

A method suitable for small samples, such as fractions from an analytical distillation, was desirable; therefore, it was decided to develop the adsorption method for a sample of 10 ml. To provide for this size sample, the column shown in figure 29 was designed. It is a modification of the column described by Mair [88] with changes in the support provided for the adsorbent, the manner of collecting samples, and the dimensions of the column.

The tip is drawn to a capillary (approximately 0.3 mm. in diameter) so that no fritted disk is required for support of the adsorbent and remixing of the desorbed material as it leaves the column is reduced. This is an important factor in obtaining a sharp break between plateaus of the adsorptogram when small fractions are collected. As no provision is made for interrupting the flow of liquid from the column, fractions must be collected continuously for the duration of an analysis.

In order to reduce the size of the column, the time required for an analysis, and the handling loss, it is desirable to use the smallest quantity of adsorbent that will consistently give a satisfactory separation of the groups of compounds. To determine this quantity, several series of analyses using different quantities of adsorbent were made on samples of shale-oil naphtha and on synthetic mixtures containing up to 90 pct. olefins or 90 pct. aromatics. Each series consisted of analyzing several samples of the same material using an increased quantity of adsorbent for each successive sample until the components were satisfactorily separated. Figure 31 illustrates the procedure with results obtained on a shale-oil naphtha using 35 and 50 g. of silica gel. The larger quantity of adsorbent gave a greater recovery of saturates. Curves obtained on this sample with more than 50 g. of gel were essentially the same as that shown in figure 31–*B*. Although the amount of silica gel needed to give a satisfactory separation varied with the composition of the sample being analyzed, 50 g. was in all cases sufficient; therefore, this amount was specified for use in the method.

Major questions concerning the reliability of the method were: Could olefins be quantitatively recovered from an acidic adsorbent? What would be the effect of nonhydrocarbon constituents in the sample? These problems were investigated by using synthetic samples [89] and by comparing results obtained by applying several different methods of analysis to a number of shale-oil and petroleum naphthas. [90]

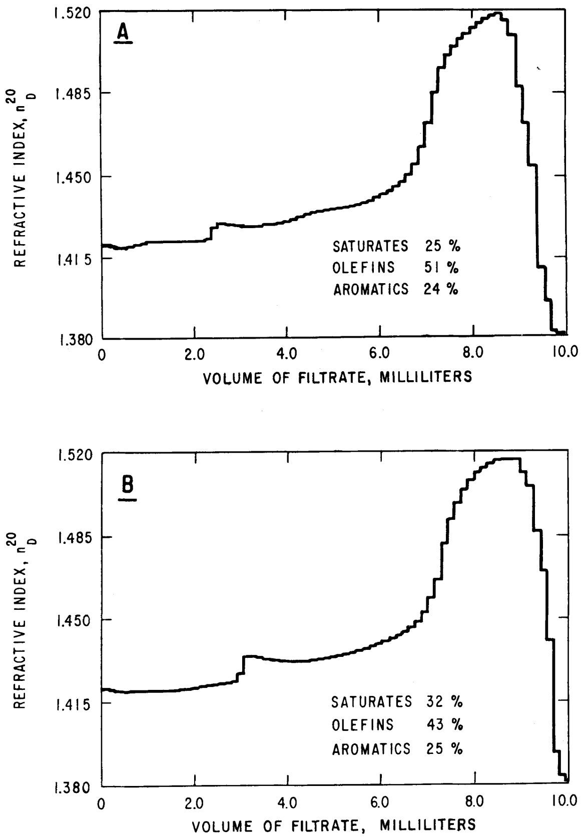

FIGURE 31.—Analysis of Shale-Oil Naphtha Using Different Quantities of Silica Gel (A—35 g., B—50 g.).

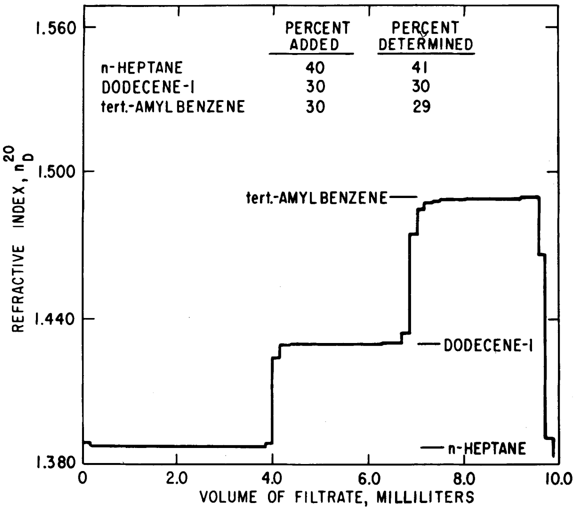

FIGURE 32.—Analysis of Hydrocarbon Mixture Containing an Olefin.

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[88] Mair, B. J., Separation and Determination of Aromatic and Monoolefin Hydrocarbons in Mixtures With Paraffins and Naphthenes by Adsorption: Jour. Res., Nat. Bureau of Standards, vol. 34, 1945, pp. 435–451.

[89] Work cited in footnote 82, p. 59.

[90] Dinneen, G. U., Smith, J. R., and Ball, John S., Olefins in Naphthas: Petrol. Ref., vol. 29, May 1950, pp. 129–134.

Results given in figures 32, 33, and 34 for a number of synthetic samples show complete recovery, within the precision of the method, of the added olefin in every instance. Also, the refractive index of the olefin plateau is close to that of the pure compound, indicating absence of contamination by other components of the mixture.

The results in figure 33 show that sulfur compounds are more strongly adsorbed than aromatics. Furthermore, there are differences in adsorbability among the classes of sulfur compounds. These differences, however, are not as great as those exhibited by the various groups of hydrocarbons. Thiophene and its homologs are only slightly more strongly adsorbed than the aromatics of corresponding boiling range; therefore, the aromatic plateau slopes gradually upward but does not closely approach the value for the refractive index of the particular thiophene homolog present (fig. 33–*A*). The adsorption of thiols and disulfides is sufficiently greater than that of aromatics to

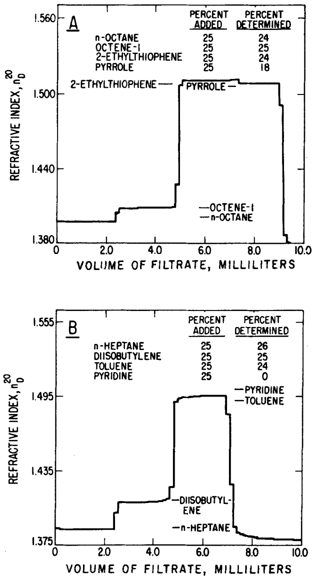

FIGURE 34.—Analyses of Mixtures Containing Nitrogen Compounds.

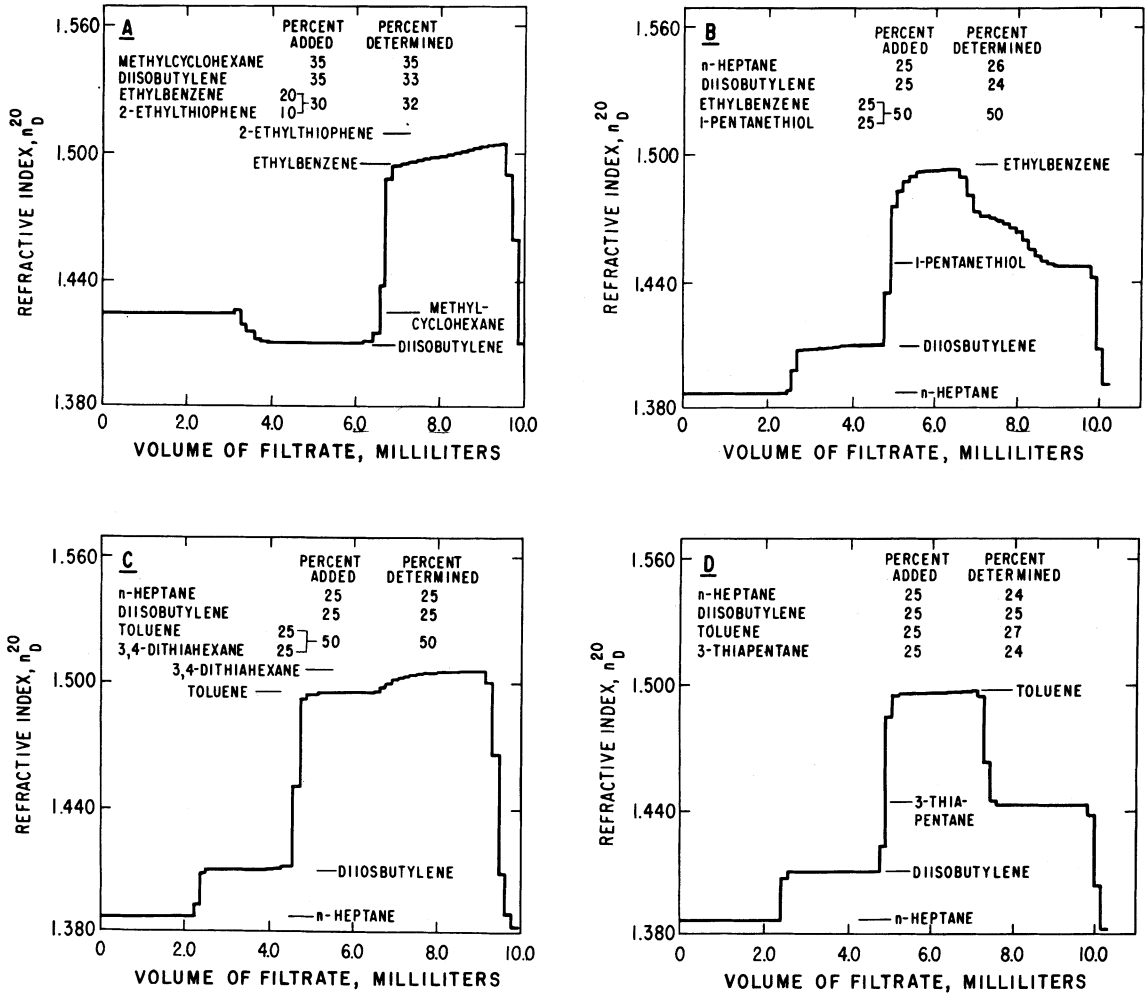

FIGURE 33.—Analyses of Mixtures Containing Sulfur Compounds.

give a distinct plateau at the refractive index of the given sulfur compound (figs. 33–*B* and 33–*C*), although the preceding break is not sharp. Sulfides, both aliphatic such as 3-thiapentane and cyclic such as 2-methylthiacyclopentane, are so strongly adsorbed that the separation between the sulfide and the aromatic is as sharp as the breaks between the various groups of hydrocarbons (fig. 33–*D*). As the sulfur compounds are usually found in the aromatic plateau, the correction for them given previously is necessary in order to calculate the quantity of aromatic hydrocarbons in a sample.

The two most abundant types of nitrogen compounds in shale-oil naphtha are pyridines and pyrroles. Synthetic samples containing the parent member of each of these groups were run with the results shown in figure 34. The pyrrole was more strongly adsorbed than the 2-ethylthiophene but was recovered in the analysis (fig. 34–*A*). The pyrrole used was not purified, which presumably accounts for the rather large loss shown. The pyridine was so strongly adsorbed that it did not appear in the filtrate, even though a number of fractions were taken after essentially pure desorbing liquid had been obtained (fig. 34–*B*). This is the reason the method specifies that the tar bases be removed by acid extraction before the adsorption analysis is made. A correction for the residual nonextractable nitrogen compounds is made in the same manner as for sulfur compounds.

The second technique for estimating the adequacy of the adsorption method was by comparing results when 10 shale-oil and 9 petroleum naphthas were analyzed for olefins by 3 direct methods based on different principles. As a check on these methods, the olefins also were determined by difference, as such a procedure is independent of many of the interferences encountered in the direct methods. The direct methods used were: Bromine number[91] using a molecular-weight correlation[92] to convert to percent olefins, nitrogen tetroxide absorption,[93] and silica-gel adsorption as described herein. The results of analyses by these direct methods are given in table 55, which also includes results for olefins determined by difference as described in the next paragraph.

The saturates were obtained as the residue from an absorption with sulfuric acid-phosphorous pentoxide reagent.[94] The aromatics

TABLE 55.—*Olefins by various methods*

| Sample No. | Olefins, pct. | | | |
|---|---|---|---|---|
| | From bromine number | From nitrogen tetroxide | From silica gel | By difference as shown in table 56 |
| SHALE-OIL NAPHTHAS | | | | |
| 1 | 70 | 51 | 47 | 49 |
| 2 | 63 | 47 | 43 | 44 |
| 3 | 69 | 53 | 48 | ---------- |
| 4 | 67 | 50 | 46 | 49 |
| 5 | 79 | 50 | 48 | 48 |
| 6 | 76 | 47 | 48 | 47 |
| 7 | 74 | 56 | 57 | 56 |
| 8 | 47 | 33 | 33 | 29 |
| 9 | 47 | 32 | 31 | 29 |
| 10 | 96 | 62 | 61 | 64 |
| PETROLEUM NAPHTHAS | | | | |
| 11 | 16 | 13 | 13 | 11 |
| 12 | 24 | 18 | 18 | 18 |
| 13 | 26 | 19 | 20 | 21 |
| 14 | 29 | 23 | 22 | 22 |
| 15 | 37 | 32 | 26 | 28 |
| 16 | 51 | 37 | 43 | 37 |
| 17 | 51 | 39 | 40 | 41 |
| 18 | 57 | 45 | 44 | 41 |
| 19 | 59 | 48 | 47 | 43 |

TABLE 56.—*Olefins by difference, in volume-percent*

| Sample No. | Saturates | | Aromatics | | | Olefins, by difference [2] |
|---|---|---|---|---|---|---|
| | By acid absorption | By silica gel | By specific dispersion [1] | By aniline point | By silica gel | |
| SHALE-OIL NAPHTHAS | | | | | | |
| 1 | 29 | 28 | ---------- | 22 | 25 | 49 |
| 2 | 34 | 32 | ---------- | 22 | 25 | 44 |
| 3 | 29 | 27 | ---------- | ---------- | 25 | ---------- |
| 4 | 32 | 33 | ---------- | 19 | 21 | 49 |
| 5 | 35 | 33 | ---------- | 17 | 19 | 48 |
| 6 | 36 | 37 | ---------- | 17 | 15 | 47 |
| 7 | 20 | 20 | ---------- | 24 | 23 | 56 |
| 8 | 58 | 55 | ---------- | 13 | 12 | 29 |
| 9 | 57 | 56 | ---------- | 14 | 13 | 29 |
| 10 | 14 | 15 | ---------- | 22 | 24 | 64 |
| PETROLEUM NAPHTHAS | | | | | | |
| 11 | 86 | 85 | 2 | 3 | 2 | 11 |
| 12 | 67 | 67 | 16 | 15 | 15 | 18 |
| 13 | 74 | 77 | 3 | 6 | 3 | 21 |
| 14 | 72 | 73 | 6 | 6 | 5 | 22 |
| 15 | 60 | 61 | 12 | 12 | 13 | 28 |
| 16 | 34 | 30 | 24 | 35 | 27 | 37 |
| 17 | 45 | 41 | 17 | 11 | 19 | 41 |
| 18 | 42 | 43 | 18 | 16 | 13 | 41 |
| 19 | 39 | 38 | 17 | 19 | 15 | 43 |

[1] The shale-oil naphthas were so dark that accurate refractive index values could not be obtained for the calculation of specific dispersion.

[2] The olefins were calculated using results for paraffins and cycloparaffins by acid absorption and, where possible, an average for aromatics by specific dispersion and aniline point. Inclusion of results by silica gel would, of course, tend to make the calculated olefins check those determined directly by silica gel.

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[91] Johnson, H. L., and Clark, R. A., Procedure for Determination of the Bromine Number of Olefinic Hydrocarbons: Anal. Chem., vol. 19 1947, pp. 869–872.

[92] Mills, I. W., Hirschler, A. E., and Kurtz, S. S., Jr., Molecular Weight-Physical Property Correlation for Petroleum Fractions: Ind. Eng. Chem., vol. 38, 1946, pp. 442–450.

[93] Bond, G. R., Jr., Determination of Olefinic Unsaturation, Nitrogen Tetroxide Method as Applied to Petroleum Hydrocarbons in the Gasoline Boiling Range: Ind. Eng. Chem., anal. ed., vol. 18, 1946, pp. 692–696.

[94] Mills, I. W., Kurtz, S. S., Jr., Heyn, A. H. A., and Lipkin, M. R., Determination of Total Aromatic Plus Olefin by Sulfonation in the Presence of Phosphorous Pentoxide: Anal. Chem., vol. 20, 1948, pp. 333–338.

were determined both by dispersion[95] [96] and by aniline point.[97] Results are shown in table 56. This table also includes results for saturates and aromatics by the silica-gel method. These results were not used, of course, in calculating the olefins by difference. However, direct comparison of the results obtained for hydrocarbon groups other than olefins aids in establishing the source of discrepant results.

The results by the nitrogen tetroxide and silica-gel methods check within the limits of accuracy of the individual methods on 13 of the samples. The greatest difference between values on any of the other samples is 6. The results calculated from bromine number, however, are 3 to 35 units higher than by either of the other methods. The first two methods give results in volume-percent, whereas the bromine-number procedure gives weight-percent. However, this does not introduce a significant error into the comparison. The differences in results increase with increasing olefin content and are greater on the shale-oil naphthas than on the petroleum naphthas. This latter fact is due primarily to the presence of sulfur and nitrogen compounds in the shale-oil naphthas. The possible extent of interference by these compounds is illustrated by the data for sulfur compounds in figure 35 and for nitrogen compounds in table 57. As shown in the figure, the bromine number for the majority of sulfur compounds tested varies directly over a considerable range with the amount of bromide-bromate reagent added. This variation ranges from 20 to 300 pct. Thus, within the limits of the procedure, varying quantities of bromine absorption, amounting in some cases to more than seven atoms per mole of sulfur compound, may be obtained. The results given in table 57 show that the bromine numbers of pyrroles are extremely high, whereas those for pyridines are negligible.

The olefins obtained by difference and shown in the last column of table 55 check well with those by nitrogen tetroxide and silica-gel methods. This also indicates that the values in the lower range are nearer the actual olefin contents than are the high values given by bromine number. Therefore, the adsorption method was deemed to be the most desirable of those available.

The adsorptogram gives plateaus corresponding to total saturates and olefins. In order to subdivide these groups into aliphatic and cyclic compounds, the adsorption method is supplemented by a calculation, given previously, utilizing refractive index and boiling point. Development of the calculation will be described

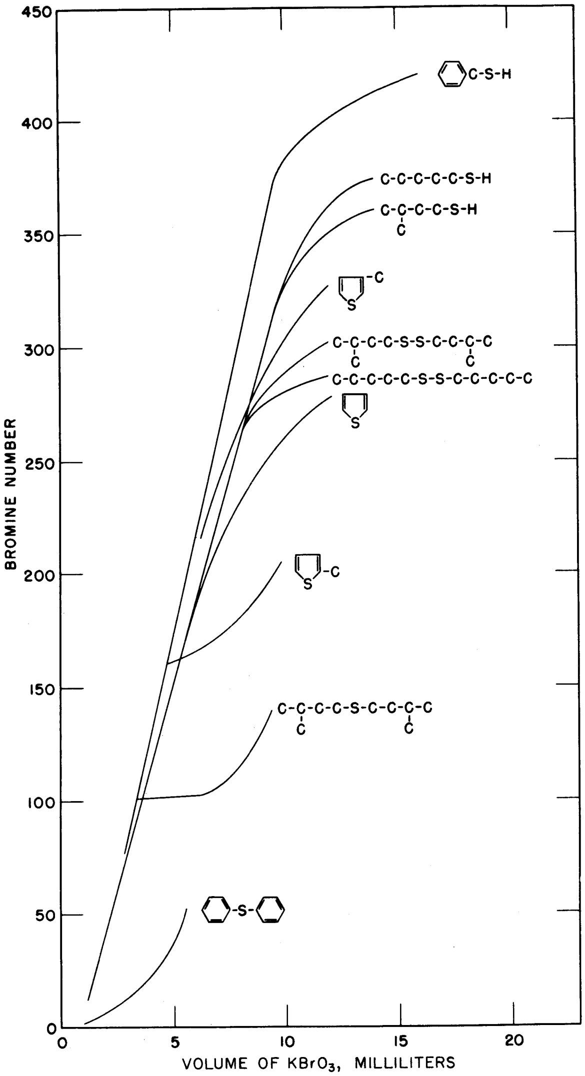

FIGURE 35.—Apparent Bromine Numbers of Sulfur Compounds.

TABLE 57.—*Bromine numbers of nitrogen compounds*

| Compound | Bromine No. |
|---|---|
| Pyrrole | 700 |
| 1-Ethylpyrrole | 528 |
| 2,5-Dimethylpyrrole | 635 |
| Pyridine | 0. 0 |
| 4-Methylpyridine | . 1 |
| 2-(5-Nonyl)pyridine | 1. 5 |
| 2,4,6-Trimethylpyridine | 1. 4 |

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[95] Grosse, A. V., and Wackher, R. C., Quantitative Determination of Aromatic Hydrocarbons by New Method: Ind. Eng. Chem., anal. ed., vol. 11, 1939, pp. 614–624.

[96] Thorne, H. M., Murphy, Walter, and Ball, John S., Determination of Aromatics in Light Petroleum Distillates by Use of Specific Dispersions Between Sodium D Line and Mercury g Line: Ind. Eng. Chem., anal. ed., vol. 17, 1945, pp. 481–486.

[97] Institute of Petroleum, Standard Methods for Testing Petroleum and Its Products: London, 9th ed., 1948. Aniline point (I.P.–2/47) pp. 7–15; aromatic content (I.P.—3/42) pp. 16–20; bromine number (I.P.–9/42) pp. 46–48.

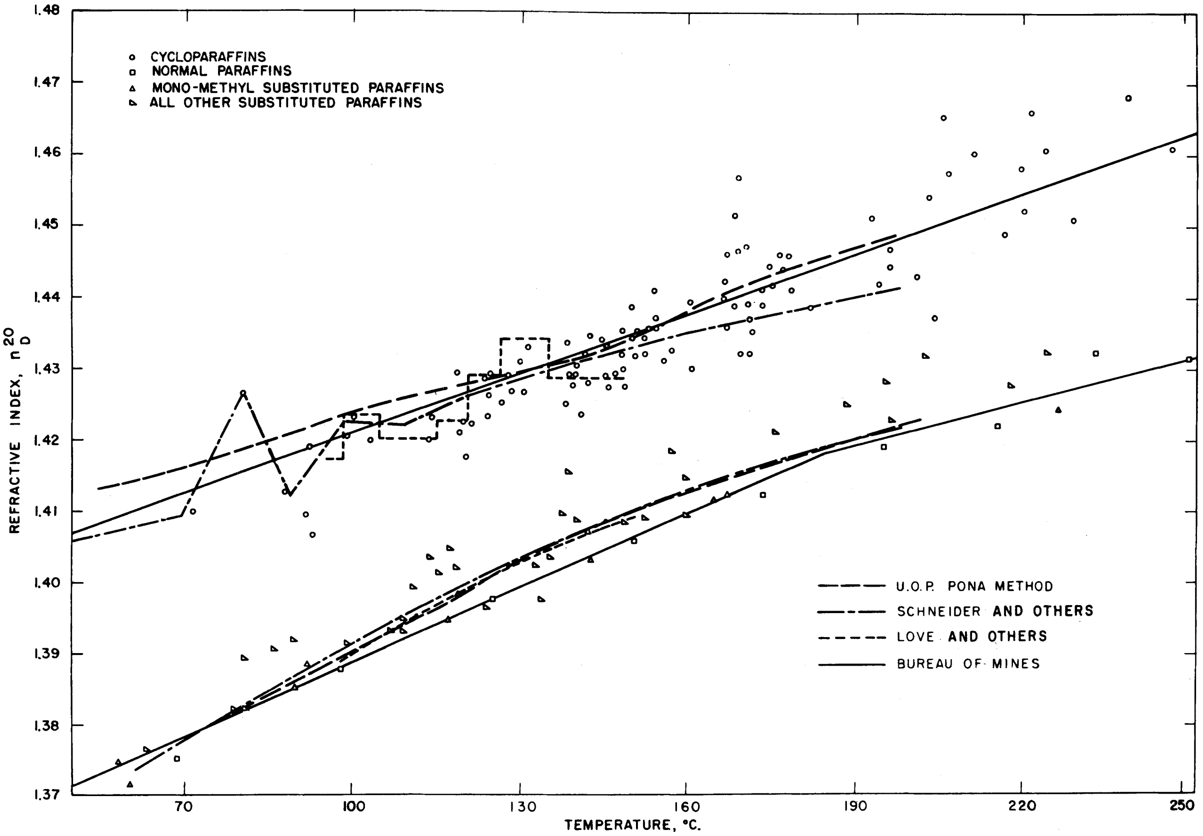

FIGURE 36.—Refractive Index Versus Boiling Point for Paraffins and Cycloparaffins.

for the saturates and is analogous for the olefins. From the boiling point of the fraction the average refractive indices of the paraffins and cycloparaffins that would be present are estimated. Using these values and the refractive index of the mixture of paraffins and cycloparaffins in the fraction, the relative amount of each type of compound is calculated. The calculation is similar to those proposed by previous investigators[98-1] but differs from them in that the refractive index of the paraffin-cycloparaffin group is determined from the adsorptogram and simplified equations are used for estimating the refractive indices of the paraffins and cycloparaffins from boiling-point data.

The refractive index at the midpoint of the saturate plateau on the adsorptogram is used in the calculation as the value representing the mixture of paraffins and cycloparaffins in the sample. A midpoint value is simple to obtain, and results on a large number of samples indicate that it will not differ from the arithmetic average of the fractions by more than ±0.0010. Furthermore, as the break between adjacent plateaus is not infinitely sharp, complete exclusion of the effect of olefins on the arithmetic average is difficult.

Figure 36 shows the lines used in developing relationships for estimating refractive indices of paraffins and cycloparaffins from boiling points. The figure gives the lines proposed by other investigators and data on some compounds that have been identified from midcontinent crude oil.[2] Although curves give the best approximation, it was thought that sufficient accuracy could be obtained using the more conveniently handled straight lines. The equations for these lines in figure 36, which are used for fractions having midboiling points of 190° C. and below, are:

Paraffin line $n_D^{20}=0.000346t+1.354$
Cycloparaffin line $n_D^{20}=0.000279t+1.393$

where $t$ is the temperature in degrees centigrade.

For fractions with midboiling points above 190° C., the same cycloparaffin line was used, but the following paraffin line with lower slope was used:

$$n_D^{20}=0.000187t+1.384.$$

---

[98] Love, R. M., Padgett, A. R., Seyfried, W. D., and Singleton, H. M., Determination of Aromatics and Naphthenes in Complex Hydrocarbon Mixtures Containing Olefins: Anal. Chem., vol. 19, 1947, pp. 37–42.

[99] Schneider, V., Stanton, G. W., and Watkins, E., A Method of Gasoline Analysis: Refiner Nat. Gas Mfr., vol. 18, March 1939, pp. 112–117.

[1] Universal Oil Products Co., Laboratory Test Methods for Petroleum and Its Products: 1947, pp. H-45–H-59.

[2] Rossini, F.D., Hydrocarbons in Petroleum: Petrol. Eng., vol. 18, January 1947, pp. 58–64.

The paraffin lines are lower, that is, nearer the values for the normal compounds, than would be obtained by averaging the values for the isomers. This location was selected because the paraffins in shale-oil naphthas are predominantly the normal compounds. The cycloparaffin line was placed at the approximate average of the available data.

Results obtained by the proposed method are compared in table 58 with those obtained on the same samples by a method[3] based on determinations of refractivity intercept and density. These latter determinations are made on the paraffin-cycloparaffin raffinate from a naphtha that has been extracted with sulfuric acid-phosphorous pentoxide reagent, and it is stated that duplicate determinations usually will not differ from the average by more than ±5. Duplicate determinations by the method described in this paper should vary from the average by not more than ±3 pct. Inspection of the data in table 58 shows that results by the two methods generally check within the limits claimed for the individual methods. It may be concluded that the methods give results of comparable accuracy.

Shale-oil naphthas may contain up to 15 pct. of tar acids and tar bases. Because these materials are adsorbed to about the same degree as the desorbing alcohol used in the adsorption method, a sample containing them gives an adsorptogram similar to that shown in figure 37. The break at the end of the curve is very gradual and there is a large loss of sample. Hence, reproducibility of results will be poor, and they will be essentially on the basis of the neutral oil rather than on the basis of the sample as charged. It is, therefore, recommended in the method that tar acids and tar bases be removed by extraction before the adsorption run is made.

TABLE 58.—*Comparison of results by proposed and refractivity-intercept methods, in volume-percent*

| Sample No. | Paraffins | | Cycloparaffins | |
|---|---|---|---|---|
| | By proposed method | By refractivity intercept | By proposed method | By refractivity intercept |
| SHALE-OIL NAPHTHAS | | | | |
| 1 | 16 | 23 | 11 | 6 |
| 2 | 27 | 27 | 6 | 8 |
| 3 | 35 | 36 | 2 | 0 |
| 4 | 16 | 15 | 4 | 5 |
| 5 | 25 | 21 | 7 | 13 |
| 6 | 26 | 28 | 7 | 4 |
| PETROLEUM NAPHTHAS | | | | |
| 7 | 71 | 66 | 22 | 24 |
| 8 | 34 | 29 | 4 | 10 |
| 9 | 62 | 64 | 11 | 8 |
| 10 | 64 | 61 | 13 | 13 |
| 11 | 70 | 77 | 25 | 18 |
| 12 | 69 | 70 | 26 | 24 |
| 13 | 31 | 33 | 7 | 9 |
| 14 | 37 | 35 | 9 | 10 |
| 15 | 68 | 71 | 17 | 15 |
| 16 | 36 | 36 | 15 | 18 |
| 17 | 52 | 53 | 15 | 14 |
| 18 | 30 | 34 | 0 | 0 |

## NITROGEN BY KJELDAHL METHOD

Much of the nitrogen in shale oil is present in pyridine-ring structures, which are considered especially refractory to decomposition by digestion in the Kjeldahl method. In order to obtain information as to the actual difficulty of determining nitrogen in shale oil and to indicate the method offering the most promise for its successful determination, an exchange program was undertaken involving 17 laboratories. Each laboratory determined nitrogen in each of three samples by procedures customarily used in that laboratory. Results obtained are shown in figure 38, grouped according to the method used.

The wide scattering of results shows that satisfactory values are not apt to be obtained by routine application of methods that do not specifically take into account the refractory nature of shale oil. However, the Kjeldahl macro-method, which is the easiest to apply on a routine basis, gave slightly the best results. By a critical study of the operating conditions, a Kjeldahl procedure was developed that proved to be satisfactory for analyzing shale oils for nitrogen content. Because close attention to procedure is necessary to attain satisfactory results, more explicit directions than usual are given.

The following apparatus is employed:

Kjeldahl digestion and distillation rack with fume exhaust or equivalent.
Kjeldahl digestion flask, 800-ml.
Erlenmeyer flask, 500-ml.
Buret, 50-ml., graduated in tenths of a milliliter.
Buret, 10-ml., graduated in twentieths of a milliliter.
Glass beads, 5-mm.-diameter.
Crucibles, porcelain, small, for example, Coors 00000 size.
Pipet or dropper, weighing.

Reagents include:

Sulfuric acid, concentrated, reagent-grade.
Potassium sulfate, reagent-grade.
Mercury, clean metallic.
Sodium hydroxide-sodium sulfide aqueous solution, 40 pct. sodium hydroxide (c.p. or a grade suitable for Kjeldahl determinations) and 3 pct. sodium sulfide nonahydrate (c.p.).
Boric acid solution, saturated.
Sulfuric acid, 0.1 N, or, for samples containing less than 0.2 pct. nitrogen, 0.01 N, standardized to four significant figures.

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[3] American Society for Testing Materials, Emergency Method of Test for Olefins, Aromatics, Paraffins, and Naphthenes in Aviation Gasoline (ES-45a): 1945 supp. to ASTM Standards, pt. 3, Philadelphia, Pa., 1945, pp. 153-166.

Methyl purple indicator (not methyl violet), aqueous solution, approximately 0.1 pct. active constituent.
Zinc, mossy.
Sucrose.

**Procedure.**—The following reagents are introduced into a Kjeldahl flask: 20±1 g. of potassium sulfate, 1.3±0.2 g. of mercury (the appropriate number of drops of mercury approximating this amount delivered from a suitable dispenser is a convenient means of measurement and addition), and approximately half of 30±1 ml. of concentrated sulfuric acid. The acid is added slowly while the flask is inclined and rotated in order to wet its inner surface. A 1-g. sample of oil weighed to the nearest 0.0001 g. is introduced into the flask. The sample should not be allowed to come in contact with the neck of the flask. Volatile liquids are best handled in some form of weighing dropper, pipet, or bulb. Solids and liquids of low volatility may be weighed conveniently in small porcelain crucibles. The sample and crucible are introduced together into the flask, where the crucible is allowed to remain during the digestion and subsequent distillation. After introduction of the sample, the neck of the flask is washed down with the remaining half of the concentrated sulfuric acid.

The flask is swirled to facilitate mixing the contents. Two or three glass beads are added to promote smooth boiling. The charged flask is placed on a digestion rack or in a fume hood. Low heat (electrical heating is preferred for uniformity and convenience) is applied until frothing has stopped. During the frothing period the flask is rotated frequently to allow uniform charring of the sample. Intermediate heat is applied for 10±2 min. to raise the temperature gradually. Finally, sufficient heat is applied so that the flask contents are brought to a rapid boil. The rate of boiling should be such that the condensation of sulfuric acid vapors proceeds approximately one-third of the way up the neck of the flask.

After a time, the flask contents will have cleared sufficiently for the individual turns of the heating element to be seen through the liquid. The final phase of the digestion is timed from this point and is allowed to proceed for 60±15 min. at the previously stated rate of boiling. The heater is turned off, but the flask should remain in the fume duct or hood until the evolution of fumes has ceased. The flask is then removed from the heater and further cooled in air or by immersing the bulb in water.

Approximately 100 ml. of a 400±10 ml. quantity of distilled water is added to the flask, and the contents are swirled until the salt cake is substantially dissolved. The balance of the distilled water is added.

Two or three small pieces of mossy zinc are added to the diluted, cooled contents of the flask. A 100±5 ml. quantity of sodium hydroxide-sodium sulfide solution is poured down the inclined neck of the flask so that a layer forms on the bottom. This is not difficult to accomplish, but failure to maintain discrete layers may lead to violent reaction, with ejection of part of the contents of the flask, or to loss of ammonia.

The flask is connected to the distillation condenser under the outlet of which a 500-ml. Erlenmeyer flask containing 25 ml. of boric acid solution and 5 drops of methyl purple indicator solution has been placed so that the tip of the condenser is well beneath the surface of the liquid. The contents of the Kjeldahl flask are mixed by swirling. Should the boric acid-methyl purple solution be drawn over into the distillation flask (a rare occurrence), no real harm is done. Another charge of boric acid and indicator is added to the receiver before distillation is started.

Heat is applied to the distillation flask, so that rapid boiling is established and maintained. When the volume of liquid in the receiving flask reaches approximately 130 ml., the receiver is lowered to expose the condenser tip, which is rinsed with distilled water. After about 1 min. of additional distillation, the heater is turned off and the condenser tube allowed to drain. For convenience in titration, the total volume in the receiver should not exceed 150 ml. The solution in the receiver is titrated with standard sulfuric acid until the green color fades into grey and just beyond to the point that the grey assumes the first faint tinge of purplish pink. The methyl purple indicator is superior in end-point sharpness to methyl red, bromocresol green, or their mixture, particularly when 0.01 N standard acid is used.

Blank determinations using 1 g. of sucrose instead of the usual sample are made each time a new lot of any of the reagents is employed.

**Discussion.**—As shown in figure 38, a number of laboratories obtained closely checking and apparently accurate results by the Kjeldahl method. However, the equal number of widely divergent results indicates that certain requirements must be met in order to obtain satisfactory results. From critical evaluations of the method conducted independently, Union Oil Co. of California, Brea, Calif., and the Bureau of Mines, Laramie, Wyo., concluded at about the same time that temperature is one of the most important factors in Kjeldahl digestions. The present method was developed as a cooperative project of these laboratories.

From consideration of the compounds likely to be present in shale oil or petroleum, pyridine was selected as probably the most refractory.

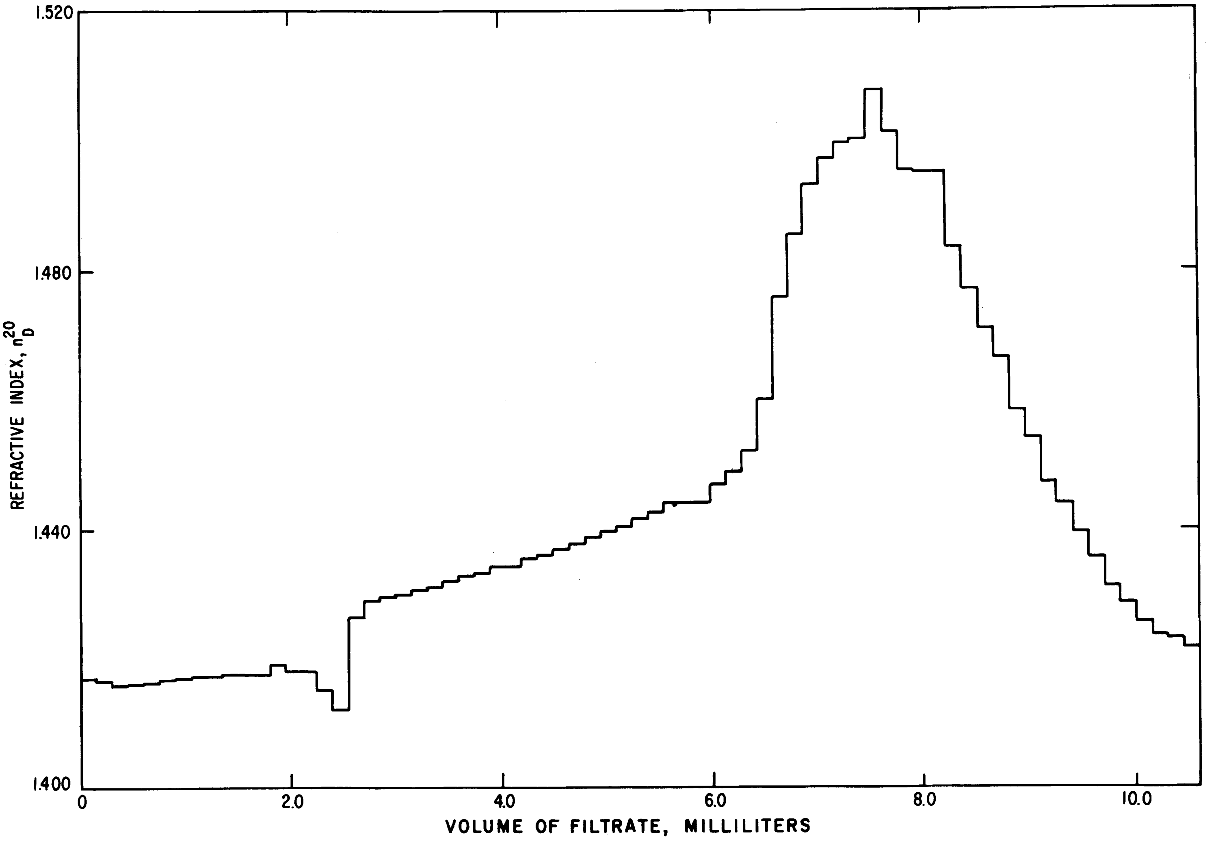

FIGURE 37.—Adsorptogram of Raw N-T-U Naphtha.

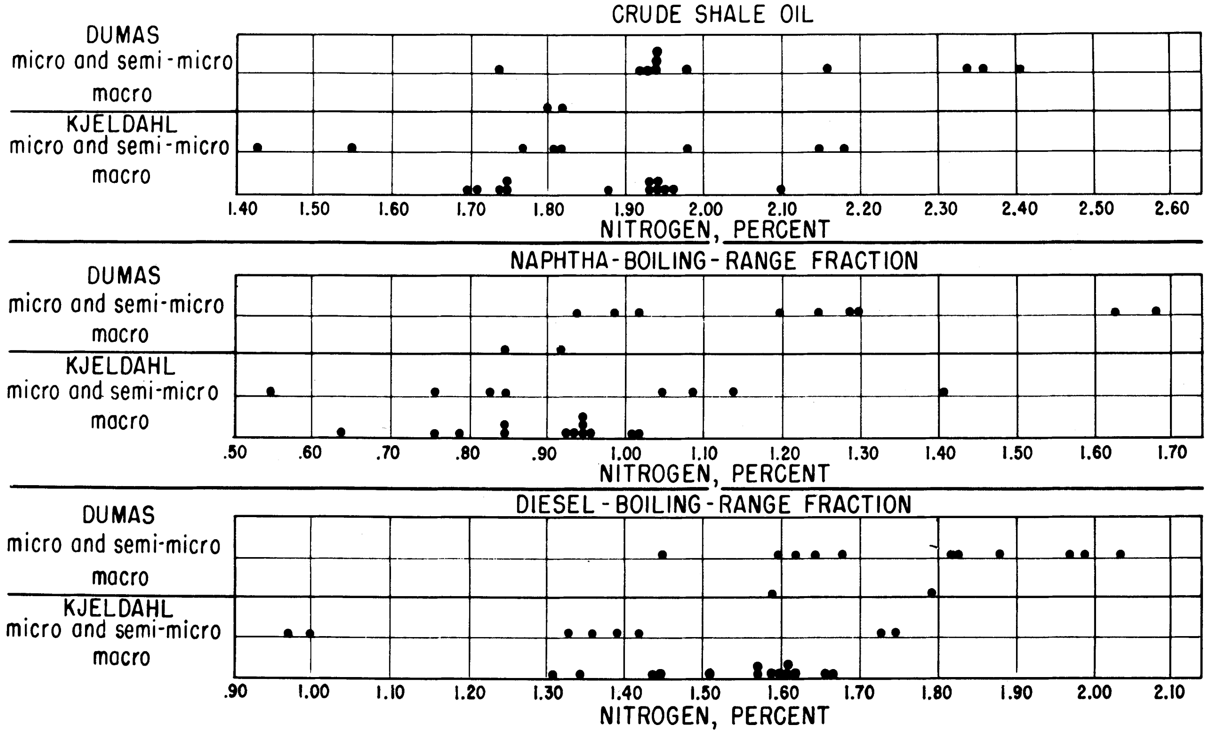

FIGURE 38.—Results Obtained in Exchange Program for Nitrogen Analysis.

TABLE 59.—*Retention of ammonium ions of ammonium oxalate as a function of digestion temperature*

| Temperature of digestion, ° C. | | Apparent nitrogen, pct. |
|---|---|---|
| After preboil | After 60-min. digestion | |
| 322 | 322 | 19.61 |
| 353 | 351 | 19.63 |
| 399 | 401 | 19.62 |
| 445 | 515 | 8.05 |
| 515 | (1) | 13.11 |

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[1] Digest solidified after 32 min., so digestion was stopped.

A solution of pyridine was prepared in a hydrocarbon solvent that was low in nitrogen. Nitrogen determinations were made on this sample by the method described, except that the amount of potassium sulfate was varied in order to change the digestion temperatures. These temperatures were measured by thermocouples in glass wells adjusted so that the junctions were immersed to a maximum depth in the pool of liquid when the flasks were inclined in digestion position. The nitrogen as determined is plotted against digestion temperature in figure 39. It is apparent that satisfactory recovery is not attained below 360° C. with 1-hr. digestion, and that 370° C. gives only a reasonable margin of safety.

A simulated digestion study was made with ammonium oxalate to determine the maximum temperature at which ammonium ions would be quantitatively retained. Results in table 59 show that rapid loss of sulfuric acid occurred on the last two samples, as evidenced by the temperature rise during the digestion period. This was accompanied by loss of nitrogen, indicating that about 400° C. is the maximum safe digestion temperature.

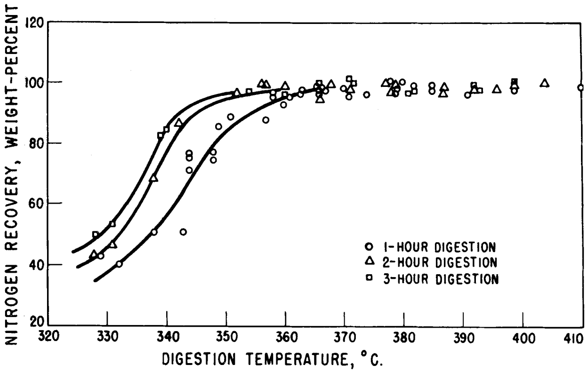

FIGURE 39.—Nitrogen Recovery Versus Digestion Temperature.

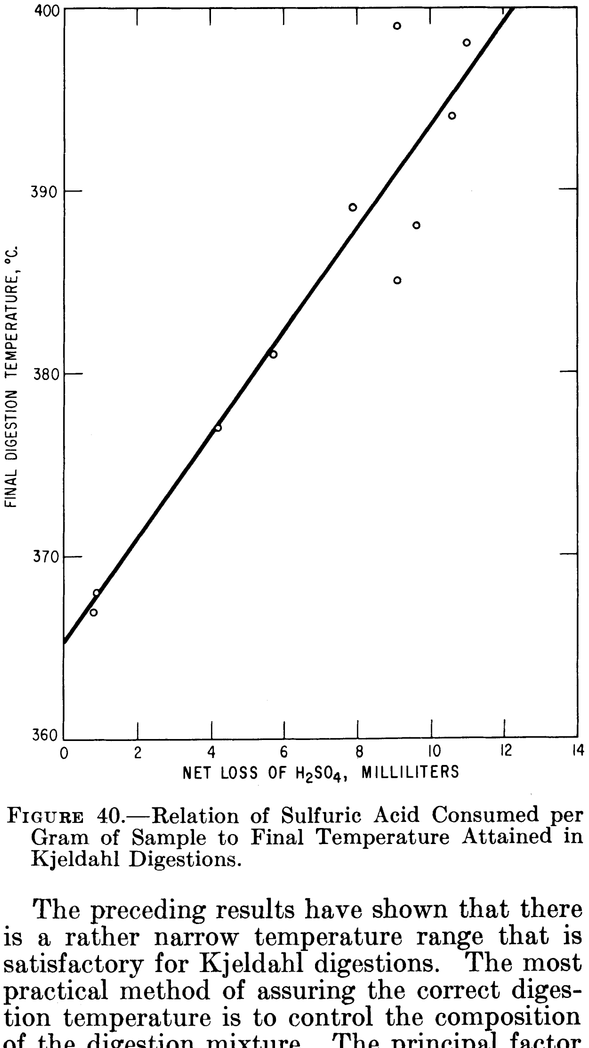

FIGURE 40.—Relation of Sulfuric Acid Consumed per Gram of Sample to Final Temperature Attained in Kjeldahl Digestions.

The preceding results have shown that there is a rather narrow temperature range that is satisfactory for Kjeldahl digestions. The most practical method of assuring the correct digestion temperature is to control the composition of the digestion mixture. The principal factor affecting this composition during digestion is the amount of sulfuric acid consumed by oxidation of the sample. With the same starting mixture the final digestion temperature achieved is, in general, a direct function of the amount of acid consumed as shown by the data in figure 40. These values were obtained in runs made with 30 ml. of sulfuric acid, 25 g. of potassium sulfate, 5 drops of mercury, and 1±0.05 g. of various types of sample. The reported loss is that actually occurring during digestion of the sample minus the amount lost (3.1 ml.) during a no-sample digestion.

The quantity of acid consumed varies markedly with the amount, volatility, and chemical nature of the sample. The effect of sample size is essentially eliminated by using a 1±0.05-g. sample for all analyses. For hydrocarbons that are volatile below digestion temperatures, paraffins and cycloparaffins consume very little acid, whereas olefins and aromatics consume about 10 ml./g. of hydrocarbon. This effect of compound type is apparently due to the paraffins and cycloparaffins distilling off during the preheating and digestion, with little or no oxidation taking place. The olefins and aromatics, on the other hand, react with the sulfuric acid to give a relatively nonvolatile product that is still present in the digestion mixture when the temperature reaches a level where oxidation takes place. By assuming that products of the oxidation reaction are carbon dioxide, sulfur dioxide, and water, the expected acid consumption for the compounds that oxidize can be calculated. The generally good agreement between calculated and observed values for several compounds is illustrated in table 60. As the volume of acid consumed by a gram of sample is affected only slightly by molecular weight for compounds of the same type, the maximum amount of acid that will be consumed is about 12 ml. This value agrees with the data in figure 40, which include results on shale-oil samples ranging from naphtha to crude oil as well as on pure compounds.

TABLE 60.—*Acid consumed by various types of compounds during Kjeldahl digestion*

| Compound | Acid consumed by sample, ml./g. | |
|---|---|---|
| | Observed | Calculated |
| Dodecene-1 | 11.0 | 11.1 |
| o-Xylene | 9.6 | 10.8 |
| Sucrose | 4.2 | 3.8 |

## BASIC NITROGEN

Naphtha from Colorado shale oil generally contains about 1 pct. nitrogen. Therefore, the nitrogen-containing compounds present one of the important problems in treating this material. These compounds are mainly pyridines, accompanied by smaller amounts of pyrroles and nitriles. The method described here for the determination of basic nitrogen uses a smaller sample, is more rapid, gives more reproducible results, and is applicable to a wider variety of samples than extraction with aqueous acid, which is the classical procedure for estimating this class of material.

The following apparatus is employed:

A pH meter covering a 400- to 800-mv. (millivolt) range, equipped with standard glass and calomel electrodes that are adequately shielded.

Reagents include:

Perchloric acid, 0.1 N in glacial acetic acid, standardized to three significant figures against potassium acid phthalate.

Acetic acid, glacial.

Toluene, ACS reagent-grade.

**Procedure.**—An accurately weighed sample (0.7 to 1.0 g.) is mixed with 100 ml. of glacial acetic acid in a 250-ml. beaker. If necessary, 5 to 10 ml. of toluene is added to ensure complete solution. Smaller quantities of sample may be used when the basic-nitrogen content is high. The mixture is titrated potentiometrically with adequate stirring, using standardized perchloric acid reagent. Care should be taken not to introduce water into the system. After completion of the titration, meter readings are plotted against volume of acid added to give a curve, such as that shown in figure 41. The end point is selected as indicated between inflection portions of the curve. Results are calculated as weight-percent nitrogen and, therefore, are comparable with the total nitrogen content as obtained by the Kjeldahl method.

**Discussion.**—The method is designed to permit the titration of weakly basic compounds; thus, the limit of its applicability is important. Titration of a number of nitrogen-containing compounds gave the results shown in table 61. These results indicate a sharp separation between those compounds that are titratable and those that are not. If the compounds are arranged in order of ionization constants in aqueous solution, those having constants greater than about $1 \times 10^{-11}$ are titratable. Thus a basic-nitrogen classification can be defined. It is favorable for analytical studies of shale-oil naphtha because pyridines are titratable where-

TABLE 61.—*Titratability of nitrogen-containing compounds with perchloric acid*

| Compound | Nitrogen, wt.-pct. | | Percent titratable |
|---|---|---|---|
| | Calculated | By titration | |
| Pyridine | 17.7 | 17.8 | 101 |
| 2-Methylpyridine | 15.0 | 15.1 | 101 |
| 2,6-Dimethylpyridine | 13.1 | 12.9 | 98 |
| 2,4,6-Trimethylpyridine | 11.6 | 11.7 | 101 |
| Quinoline | 10.9 | 10.7 | 98 |
| Isoquinoline | 10.9 | 10.6 | 97 |
| Acridine | 7.8 | 7.9 | 101 |
| Piperidine | 16.5 | [1] 15.7 | 95 |
| Morpholine | 16.1 | [1] 15.8 | 98 |
| Aniline | 15.0 | 15.1 | 101 |
| Benzylamine | 13.1 | 13.1 | 100 |
| Tribenzylamine | 4.9 | 4.9 | 100 |
| Tri-n-butylamine | 7.6 | 7.2 | 95 |
| α-Naphthylamine | 9.8 | 9.8 | 100 |
| Monoethanolamine | 22.9 | 22.5 | 98 |
| Aminoacetic acid | 18.7 | 18.6 | 99 |
| 2-Aminobenzothiazole | 18.7 | 9.4 | 50 |
| Pyrrole | 20.9 | .0 | 0 |
| 1-Methylpyrrole | 17.3 | .0 | 0 |
| 2,5-Dimethylpyrrole | 14.7 | .6 | 4 |
| Indole | 12.8 | .0 | 0 |
| 3-Methylindole | 10.7 | .0 | 0 |
| Carbazole | 8.4 | .0 | 0 |
| Benzoxazole | 11.8 | .0 | 0 |
| Benzotriazole | 35.3 | .1 | 0 |
| Diphenylamine | 8.3 | .0 | 0 |
| Urea | 46.7 | .0 | 0 |
| Acetamide | 23.7 | .0 | 0 |
| Allyl cyanide | 20.9 | .0 | 0 |
| Isatin | 9.5 | .0 | 0 |
| Methyl red | 15.6 | .0 | 0 |

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[1] Some loss due to fuming.

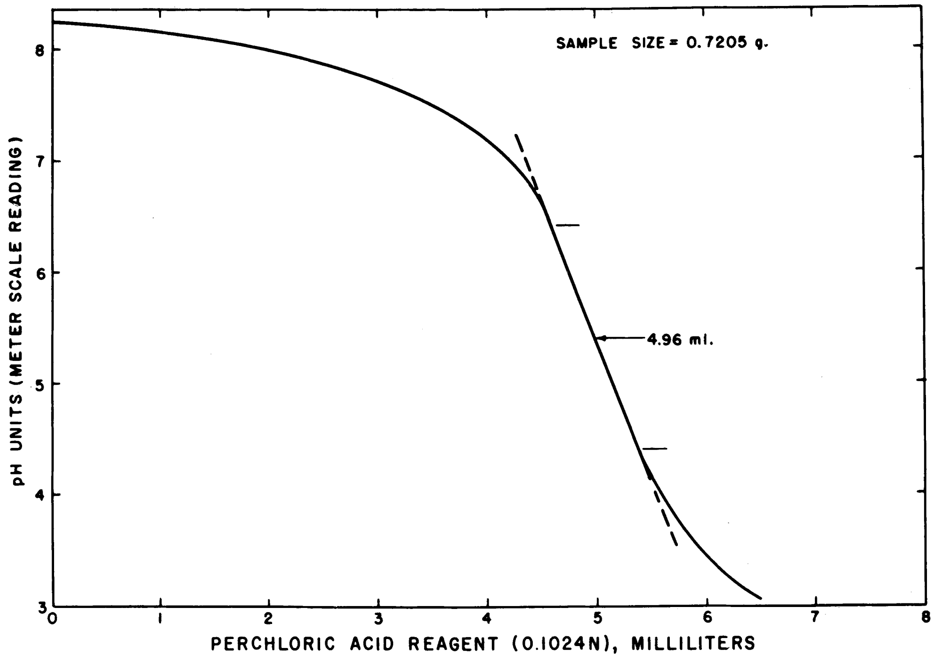

FIGURE 41.—Titration Curve—Basic Nitrogen Content of Shale-Oil Diesel Fraction.

as the majority of pyrrole homologs are not. The precision of the method was demonstrated by a series of determinations on redistilled pyridine (99.9 mole-pct. pure) that gave results averaging within 1 pct. of the theoretical value.

## IDENTIFICATION OF THIOPHENES

Thiophene and its homologs form the most abundant group of sulfur compounds in shale-oil naphthas. Because of the scarcity of reference compounds, the usual techniques of organic chemistry were not easily applicable to the identification of these compounds. A procedure based primarily on the correlation of mass spectra with molecular structure was developed for the purpose.

The following apparatus is employed:

Adsorption column, to provide an adsorbent-to-sample ratio of 30:1 and a height-to-diameter ratio of at least 50:1.

Reagents include:

Sulfuric acid, 10 pct.
Sodium hydroxide, 10 pct.
Hydrochloric acid, 10 pct.
Sodium chloride, 10 pct.
Acetic acid, 50 pct.
Silver nitrate, about 0.05 N.
Mercurous nitrate, reagent-grade.
Mercuric acetate, reagent-grade.
Ethanol, 95 pct.
Florisil, magnesium silicate manufactured by Floridin Co., activated 4 hr. at 150° C.
Pentane, any mixture of saturated hydrocarbons boiling near 100° F. and having no high-boiling residue.

**Procedure.**—The naphtha is extracted with aqueous sulfuric acid and then with sodium hydroxide to give a neutral oil that is distilled into narrow-boiling fractions. The sulfur content of each fraction is determined. The fractions are recombined on the basis of boiling point and sulfur content to separate the thiophenes of different molecular weights and at least partially the isomers within a molecular-weight group. The composite fractions are treated with 0.05 N $AgNO_3$ to remove any thiols remaining after the alkali extraction and with powdered mercurous nitrate to remove sulfides. Following these treatments the sulfur in the fractions is mostly in the form of thiophenes.

A concentrate of aromatic hydrocarbons and thiophenes is prepared from the composite fractions by adsorption. Florisil is used as the adsorbent because it permits sharp separation of the thiophenes from interfering substances such as olefins and nitrogen-containing compounds. Elution techniques are used, employing pentane and an appropriate column. The portion of the eluate containing only saturates and olefins is discarded. The eluate containing thiophenes and aromatics is stripped of solvent by distillation. The resulting concentrates normally contain over 95 pct. of the thiophenes originally in the fraction and are contaminated with only trace amounts of olefins.

Thiophenes are separated from each concentrate by preparation of their mercuric acetate derivatives. The concentrates are reacted with mercuric acetate in 50 pct. acetic acid at 60° C. Under these conditions mercuric acetate reacts with any hydrogen atom on a ring carbon. The mercuric acetate derivatives are filtered from the reaction mixture, washed, and dried. Thiophenes are regenerated from these derivatives by refluxing with 10 pct. hydrochloric acid. Repeating this procedure usually gives thiophenes containing less than 10 pct. hydrocarbon impurities, which consist mainly of aromatics. Selected properties of the isolated thiophenes are compared with those of available reference compounds. The isolation procedure may yield an individual thiophene, but is more likely to give a group of thiophene isomers, one of which is predominant.

The most satisfactory identification is the preceding direct comparison of properties of the unknown with those of an authentic reference compound. If suitable reference samples are not available, identification may still be made from correlation of structure with mass spectra, preparation of mercuric acetate derivatives, methylation, and hydrogenation. The particular combination of these techniques that is required depends on the compound under investigation. Any thiophene having a molecular weight of less than 154 may be identified, and among higher-molecular-weight compounds many of the possible structures may be eliminated from consideration.

A mass spectrum is obtained on the material regenerated from the mercuric acetate reaction. The configuration of the alkyl substituents is estimated from the following correlations involving eight selected peaks in the spectrum:

> The base or highest peak in the spectrum results from the breaking of a C–C or C–H bond once removed from the ring. Polymethyl thiophenes having the 2- or 3-positions occupied are exceptions in which the C–C bond next to the ring breaks.
>
> The parent peak (equivalent to molecular weight of compound) is greater than 50 pct. of the base peak when only methyl groups are on the ring and less than 50 pct. of the base peak for all other types of substitution.
>
> The parent-peak-less-mass-1 is greater than 50 pct. of the base peak when only methyl groups are on the ring and is 2 to 50 pct. of the base peak when methyl and ethyl or only ethyl groups are on the ring.
>
> The parent-peak-less-mass-31 is larger than the parent-peak-less-mass-29 when an isopropyl group and another group are present or when a tert-butyl group is present.
>
> The 85+ peak is 10 to 15 pct. of the base peak for monoalkyl substitution when the carbon adjacent to the ring is tertiary, is 4 to 10 pct. of the base peak for monoalkyl substitution when the carbon adjacent to the ring is secondary, and is less than 4 pct. of the base peak for all other types of substitution.
>
> The 84+ peak is larger than the 85+ peak when a single, normal alkyl group is attached to the ring.
>
> The 59+ peak is over 15 pct. of the base peak when methyl groups are in the 2- and 5-positions, is 5 to 15 pct. of the base peak when a methyl group is in the 2-position, and is less than 5 pct. when the 2- and 5-positions are unoccupied or are occupied by any alkyl group other than methyl.
>
> The 41+ peak is above 10 pct. of the base peak when a tert-butyl group or two isopropyl groups are on the ring and is less than 10 pct. of the base peak for mono-, di-, and tri-substitution when only methyl and ethyl groups are on the ring.

The mass-spectral correlations do not usually give the relative positions of the substituents on the thiophene nucleus. This information is obtained from mercuric acetate derivatives, methylation, and hydrogenation.

Mercuric acetate derivatives are prepared at 25° C. and 60° C. according to the method of Steinkopf and Killingstad [4] with the following modifications. The reaction time at 25° C. is limited to 15 min. and the quantity of mercuric acetate used is limited to the theoretical amount required to form the di-derivative. The quantity of mercuric acetate used in the 60° C. reaction is limited to the theoretical amount required to form the tri-derivative. If under these conditions no precipitate forms at 60° C., the reaction is repeated with the amount of mercuric acetate reduced to the theoretical amount required to form the di-derivative. If a precipitate still does not form, the reaction is again repeated, with the quantity of mercuric acetate reduced to that required to form the monoderivative. Repeating the reaction with different quantities of reagent is necessary because the derivatives may be soluble in an excess of mercuric acetate. Derivatives may be differentiated by determination of either mercury or sulfur content.

Mercuric acetate reacts with thiophenes at 25° C. to replace the hydrogens in the 2- and 5-positions, if any are present. If none are present, the reagent replaces hydrogens in the 3- and 4-positions. All hydrogen atoms present are replaced by mercuric acetate at 60° C. Thus, from the type of derivative formed, as shown in table 62, an unknown thiophene is classified in one of the following groups: 2-Substituted; 3-substituted; 2,5- or 3,4-disubstituted; 2,3- or 2,4-disubstituted; and 2,3,4- or 2,3,5-trisubstituted.

Within these groups, a 2,5-disubstituted thiophene is differentiated from a 3,4-disubstituted thiophene, and a 2,3,4-trisubstituted thiophene from a 2,3,5-trisubstituted thiophene, by methylation. The methylated thiophene is obtained by reduction of the aldehyde prepared by the method of King and Nord.[5] If the 59+ peak in the mass spectrum of the material after

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[4] Steinkopf, W., and Killingstad, A., Mercury Derivatives of Thiophene: Ann., vol. 532, 1937, pp. 288–293.

[5] King, W. J., and Nord, F. F., Preparation of Thiophene-2-aldehyde and Some Substituted Thiophene Aldehydes: Jour. Org. Chem., vol. 13, 1948, pp. 635–640.

TABLE 62.—*Mercuric acetate derivatives of thiophenes*

| Numbers indicate position of substituent group(s) | Type of derivative at | |
|---|---|---|
| | 25° C. | 60° C. |
| 2 | mono | tri. |
| 3 | di | tri. |
| 2,5 | di | di. |
| 3,4 | di | di. |
| 2,3 | mono | di. |
| 2,4 | mono | di. |
| 2,3,4 | mono | mono. |
| 2,3,5 | mono | mono. |

methylation is more than 1.5 times the 59+ peak in the original material, the methyl group entered the 2- or 5-position. This assumes that the methyl group will enter the 2- or 5-position if it is open. If the 59+ peak of the sample after methylation is less than 1.5 times the 59+ peak of the original, the methyl group entered the 3- or 4-position, indicating that the 2,5-positions are occupied by side chains.

A 2,3-disubstituted thiophene is usually differentiated from a 2,4-disubstituted thiophene by hydrogenation. The Raney nickel hydrogenation procedure of Blicke and Sheets [6] is used. The resulting alkane is identified by direct comparison of its mass spectrum with reference standards.

Unless the isolated thiophenes consist predominantly of one isomer, the above techniques are, of course, not applicable. Mixtures of certain isomers may be separated by taking advantage of the difference in solubility of mono- and di-mercuric chloride derivatives.[7] The mixed mercuric acetate derivatives are refluxed for 8 hr. with 10 pct. sodium chloride to form the corresponding mercuric chloride derivatives. These are dried and then extracted for 8 hr. with hot ethanol. The extraction removes the soluble mono- from the insoluble di-mercuric chloride derivatives. The thiophenes are regenerated by refluxing with dilute hydrochloric acid.

**Discussion.**—The first step in a successful identification procedure is to separate the desired components from the mixture in which they occur. In the case of shale-oil distillates this mixture is complex. A large part of the nitrogen and oxygen compounds in the naphtha can be separated from it by simple extraction techniques. Unfortunately, the thiophenes cannot be concentrated in a similar manner because reagents that react with them also react with other compounds in the naphtha. The results obtained during the development of the silica-gel adsorption method indicated that adsorption might offer a promising technique for concentrating the thiophenes. Since the object was to obtain as great a recovery as possible of the thiophenes with a minimum of contamination by olefins, an elution technique was used in preference to the displacement technique described previously. Several adsorbents were tried for this separation, and activated Florisil was selected as the most satisfactory. The adsorption separation yields a concentrate of sulfur-containing compounds and aromatic hydrocarbons. The sulfur compounds other than thiophenes are removed from this concentrate by extraction with appropriate reagents. The thiophenes are then removed by reaction with mercuric acetate and recovered by refluxing with mineral acid.

The object of the investigation for which this procedure was developed was to identify a sufficient number of individual thiophenes to establish a pattern of their occurrence and to make an estimate of their relative abundance. Data on only a few thiophene homologs are available in the literature for use in identification work. It was beyond the scope of the present investigation to provide complete background information by synthesizing all the thiophenes that might possibly be encountered. Hence, the systematic examination described in this section was devised. With the probable identification of a given compound established through this examination, final proof could be obtained, if desired, by the synthesis of only the indicated thiophene.

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[6] Blicke, F. F., and Sheets, D. G., Derivatives of Thianaphthene: Jour. Am. Chem. Soc., vol. 71, 1949, pp. 4010–4011.

[7] McKittrick, D. S., Sulfur Compounds in Pressure-Cracked Naphtha and Cracked Naphtha Sludge: Ind. Eng. Chem., vol. 21, 1929, pp. 585–592.